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(54) **SUPPORTED NONMETALLOCENE
CATALYST, PREPARATION AND USE
THEREOF**

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This patent is subject to a terminal dis-
claimer.

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USPC **526/161**; 526/160; 526/172; 526/129;
526/127; 526/130; 526/123.1; 526/124.2;
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(57) **ABSTRACT**

This invention relates to a supported nonmetallocene catalyst and preparation thereof. The supported nonmetallocene catalyst can be produced with a simple and feasible process and is characterized by an easily controllable polymerization activity. This invention further relates to use of the supported nonmetallocene catalyst in olefin homopolymerization/copolymerization, which is characterized by a lowered assumption of the co-catalyst as compared with the prior art.

22 Claims, No Drawings

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SUPPORTED NONMETALLOCENE CATALYST, PREPARATION AND USE THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a U.S. national phase application based on PCT/CN2010/001604, filed Oct. 13, 2010, which claims the priority of Chinese Application Nos. 200910180100.6, filed Oct. 26, 2009; 200910180607.1, filed Oct. 26, 2009; 200910180601.4, filed Oct. 26, 2009; and 200910180606.7, filed Oct. 26, 2009, the contents of all of which are incorporated by reference herein in their entirety.

TECHNICAL FIELD

The present invention relates to a nonmetallocene catalyst. Specifically, this invention relates to a supported nonmetallocene catalyst, preparation thereof and use thereof in olefin homopolymerization/copolymerization.

BACKGROUND ART

The nonmetallocene catalyst, also called as the post-metallocene catalyst, was discovered in middle and late 1990's, whose central atom involves nearly all of the transition metal elements. The nonmetallocene catalyst is comparative to, or exceeds, the metallocene catalyst in some aspects of the performance, and has been classified as the fourth generation catalyst for olefin polymerization, following the Ziegler catalyst, the Ziegler-Natta catalyst and the metallocene catalyst. Polyolefin products produced with such catalysts exhibit favorable properties and boast low production cost. The coordination atom of the nonmetallocene catalyst comprises oxygen, nitrogen, sulfur and phosphor, without containing a cyclopentadiene group or a derivative thereof (for example, an indene group or a fluorene group). The nonmetallocene catalyst is characterized in that its central atom shows comparatively strong electrophilicity and has a cis alkyl metal type or a metal halide type central structure, which facilitates olefin insertion and σ -bond transfer. Therefore, the central atom is easily subject to alkylation, and therefore facilitates formation of a cationic active center. The thus formed complex has a restricted geometrical configuration, and is stereoselective, electronegative and chiral adjustable. Further, the formed metal-carbon bond is easy to be polarized, which further facilitates homopolymerization and copolymerization of an olefin. For these reasons, it is possible to obtain an olefin polymer having a comparatively high molecular weight, even under a comparatively high polymerization temperature.

However, it is known that in the olefin polymerization, the homogeneous phase catalyst suffers from such problems as short service life, fouling, high consumption of methyl aluminoxane, and undesirably low or high molecular weight in the polymer product, and thus only finds limited use in the solution polymerization process or the high-pressure polymerization process, which hinders its wider application in industry.

Chinese patent Nos. 01126323.7, 02151294.9 and 02110844.7, and WO03/010207 disclose a catalyst or catalyst system finding a broad application in olefin polymerization. However, the catalyst or catalyst system should be accompanied by a comparatively high amount of co-catalysts, to achieve an acceptable olefin polymerization activity. Further, the catalyst or catalyst system suffers from such problems as short service life and fouling.

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It is normal to support the nonmetallocene catalyst by a certain process, so as to improve the performance of the catalyst in the polymerization and the particle morphology of the polymer products. This is reflected by, moderate reduction of the initial activity of the catalyst, elongation of the service life of the catalyst, alleviation or elimination of caking or flash reaction during the polymerization, improvement of the polymer morphology, and increase of the apparent density of the polymer, thus extending its use to other polymerization processes, for example, the gas phase polymerization or the slurry polymerization.

Aiming at the catalysts of the Chinese patent Nos. 01126323.7, 02151294.9 and 02110844.7, and WO03/010207, Chinese patent application Laid-Open Nos. CN1539855A, CN1539856A, CN1789291A, CN1789292A and CN1789290A, and WO2006/063501, and Chinese application patent No. 200510119401.x provide several ways to support same catalyst on a carrier so as to obtain a supported nonmetallocene catalyst. However, each of these applications relates to the technology of supporting a transition metal-containing nonmetallocene organic metallic compound on a treated carrier, which necessarily involves complicate preparation steps.

Chinese patent application Laid-Open No. CN1539856A discloses a process for supporting a nonmetallocene catalyst on a composite carrier, comprising the steps of (1) drying or baking a porous carrier (as the carrier) at 100 to 1000° C., under an inert atmosphere or under a reduced pressure for 1 to 24 hours to thermally activate same; (2) dissolving a magnesium compound in a tetrahydrofuran-alcohol mixing system to obtain a solution, and then adding the thermally activated porous carrier to the solution, to sufficiently react with each other at 0 to 60° C. under stirring to obtain a transparent system, upon filtration, washing, drying and suction drying, to obtain a composite carrier; or introducing into the transparent solution a non-polar organic solvent to sufficiently precipitate same, and then upon filtration, washing, drying and suction drying to obtain a composite carrier; (3) dissolving a nonmetallocene catalyst for olefin polymerization in a solvent, and then contacting same with the composite carrier or the modified carrier for 12 to 72 hours, upon filtration, washing, drying and suction drying, to obtain the supported nonmetallocene catalyst. According to this process, it is necessary to prepare the composite carrier at the first place and then contacting same with the catalyst solution.

Chinese patent application Laid-Open No. CN1789290A discloses a process for supporting a nonmetallocene catalyst with a high activity, comprising the steps of reacting a carrier with a chemical activating agent to obtain a modified carrier; dissolving a magnesium compound in a tetrahydrofuran-alcohol mixing system to obtain a solution, and then adding the modified carrier to the solution to conduct a react, upon filtration, washing, drying and suction drying, to obtain a composite carrier; dissolving a nonmetallocene catalyst for olefin polymerization in a solvent, and then reacting same with the composite carrier, upon filtration, washing, drying and suction drying, to obtain the supported nonmetallocene catalyst. According to this process, it is necessary to prepare the modified carrier at the first place and then reacting same with the magnesium compound to obtain the composite carrier and then contacting same with the catalyst solution.

Chinese patent application Laid-Open No. CN101423574A discloses a supported single site nonmetallocene catalyst component and the preparation process thereof, comprising the steps of (1) preparation of a magnesium chloride/silica carrier; (2) preparation of an alkyl aluminoxane/magnesium chloride/silica carrier; and (3) prepa-

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ration of the supported single site nonmetallocene catalyst component. According to this process, it is necessary to prepare the composite carrier at the first place and then reacting same with the alkyl aluminoxane, and finally contacting same with the catalyst solution.

Most of the prior art olefin polymerization catalysts are metallocene catalyst-based, for example, those according to U.S. Pat. No. 4,808,561 and U.S. Pat. No. 5,240,894, Chinese patent application Laid-Open Nos. CN1344749A, CN1126480A, CN1307594A, CN1103069A, and CN1363537A, and U.S. Pat. No. 6,444,604, EP 0685494, U.S. Pat. No. 4,871,705 and EP0206794, and Chinese patent No. 94101358.8. Again, all of these applications relate to the technology of supporting a transition metal-containing metallocene catalyst on a treated carrier.

The catalyst prepared using anhydrous magnesium chloride as a carrier exhibits a high catalytic activity in the olefin polymerization, but this kind of catalyst is very brittle, prone to crush in the polymerization reactor, resulting in a poor polymer morphology. The catalyst supported on silica has an excellent flowability, useful to a fluidized-bed gas-phase polymerization, but the silica-supported metallocene and nonmetallocene catalyst shows a lowered catalytic activity. If magnesium chloride could be appropriately combined with silica, a catalyst with high catalytic activity, controllable granule size and good abrasion resistance may be obtained.

According to EP0260130, provided is a catalyst produced by supporting a metallocene or nonmetallocene transition metal compound onto a methyl aluminoxane-treated SiO₂ carrier, wherein the nonmetallocene transition metal herein refers to ZrCl₄, TiCl₄ or VOCl₃ only. According to this patent, it is preferred for the surface of the carrier to be treated with an organic magnesium compound or the mixture of a magnesium compound and an alkyl aluminum. However, the process involved is very complicated, necessitating a vast of production steps.

Chinese patent No. 200610026765.8 discloses a single site Ziegler-Natta catalyst for olefin polymerization. In this catalyst, a coordination group-containing salicylaldehyde or substituted salicylaldehyde derivative is used as the electron donor. The catalyst is produced by introducing a pre-treated carrier (for example, silica), a metallic compound (for example, TiCl₄) and the electron donor into a magnesium compound (for example, MgCl₂)/tetrahydrofuran solution and then post-treating the resultant.

Chinese patent No. 200610026766.2 is similar to this patent, and relates to an organic compound containing a hetero atom and use thereof for producing a Ziegler-Natta catalyst.

Chinese patent application Laid-Open No. CN101412766A discloses a process for producing a magnesium compound supported nonmetallocene catalyst, comprising the steps of contacting a magnesium compound with a nonmetallocene ligand, to obtain a contact resultant, and treating the contact resultant with a chemical treating agent selected from the group consisting of Group IVB metal compounds, to obtain the magnesium compound-supported nonmetallocene catalyst. The thus obtained catalyst exhibits a relatively higher activity, however, a poor polymer particle morphology, a rather lowered bulk density and a relatively increased amount of fine powders.

As can be seen from aforesaid, the prior art supported nonmetallocene catalyst suffers from such problems as a complicate supporting process, which generally involves multiple steps for treating the carrier before supporting the nonmetallocene complex, and a low olefin polymerization activity, wherein there is no easy way to adjust same. If one

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tries to increase the activity, he has to significantly increase the amount of the co-catalyst to be used, which is undesirable. Further, the prior art supported nonmetallocene catalyst has been produced by supporting a nonmetallocene complex onto a treated carrier, and therefore is problematic in stability.

Therefore, there still exists a need for a supported nonmetallocene catalyst, which can be produced in a simple way and in an industrial scale, free of the problems associated with the prior art supported nonmetallocene catalyst.

SUMMARY OF THE INVENTION

Upon in-depth study of the prior art, the present inventors found that a supported nonmetallocene catalyst produced by using a specific process can solve the problems identified as aforesaid, whereby achieving this invention.

According to this invention, the present process for producing a supported nonmetallocene catalyst can be conducted in the absence of any proton donor or any electron donor (for example, di-ether compounds conventionally used in this field for this purpose), without the need of severe reaction requirements and reaction conditions. For these reasons, the present process is simple and suitable for industrial application.

Specifically, this invention generally relates to the first to fourth embodiments as follows.

The first embodiment relates to a process for producing a supported nonmetallocene catalyst, which comprises the steps of: dissolving a magnesium compound and a nonmetallocene complex in a solvent, to obtain a magnesium compound solution; mixing a porous carrier or a thermally activated porous carrier with the magnesium compound solution to obtain a slurry; and drying the slurry to obtain the supported nonmetallocene catalyst.

The second embodiment relates to a process for producing a supported nonmetallocene catalyst, which comprises the steps of: dissolving a magnesium compound and a nonmetallocene complex in a solvent, to obtain a magnesium compound solution; mixing a porous carrier or a thermally activated porous carrier with the magnesium compound solution to obtain a slurry; and introducing into the slurry a precipitating agent to obtain the supported nonmetallocene catalyst.

The third embodiment relates to a process for producing a supported nonmetallocene catalyst, which comprises the steps of: dissolving a magnesium compound and a nonmetallocene complex in a solvent, to obtain a magnesium compound solution; mixing a porous carrier or a thermally activated porous carrier with the magnesium compound solution to obtain a slurry; drying the slurry to obtain a composite carrier; and treating the composite carrier with a chemical treating agent selected from the group consisting of Group IVB metal compounds to obtain the supported nonmetallocene catalyst.

The fourth embodiment relates to a process for producing a supported nonmetallocene catalyst, which comprises the steps of: dissolving a magnesium compound and a nonmetallocene complex in a solvent, to obtain a magnesium compound solution; mixing a porous carrier or a thermally activated porous carrier with the magnesium compound solution to obtain a slurry; introducing into the slurry a precipitating agent to obtain a composite carrier; and treating the composite carrier with a chemical treating agent selected from the group consisting of Group IVB metal compounds to obtain the supported nonmetallocene catalyst.

More specifically, this invention relates to the following aspects.

1. A process for producing a supported nonmetallocene catalyst, comprising the steps of: dissolving a magnesium compound and a nonmetallocene complex in a solvent, to obtain a magnesium compound solution; mixing a porous carrier or a thermally activated porous carrier with the magnesium compound solution to obtain a slurry; and drying the slurry, or introducing into the slurry a precipitating agent, to obtain the supported nonmetallocene catalyst.

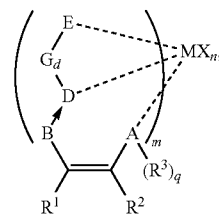
2. A process for producing a supported nonmetallocene catalyst, comprising the steps of: dissolving a magnesium compound and a nonmetallocene complex in a solvent, to obtain a magnesium compound solution; mixing a porous carrier or a thermally activated porous carrier with the magnesium compound solution to obtain a slurry; drying the slurry, or introducing into the slurry a precipitating agent, to obtain a composite carrier; and treating the composite carrier with a chemical treating agent selected from the group consisting of a Group IVB metal compound to obtain the supported nonmetallocene catalyst.

3. The process according to any of the aforesaid aspects, further comprising the step of pre-treating the composite carrier with an assistant chemical treating agent selected from the group consisting of an aluminoxane, an alkylaluminum and any combination thereof before treating the composite carrier with the chemical treating agent.

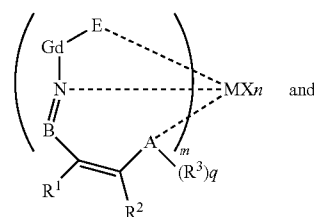
4. The process according to any of the aforesaid aspects, wherein the porous carrier is one or more selected from the group consisting of olefin homopolymers or copolymers, vinyl alcohol homopolymers or copolymers, cyclodextrins, polyesters or co-polyesters, polyamides or co-polyamides, vinyl chloride homopolymers or copolymers, acrylic ester homopolymers or copolymers, methacrylic ester homopolymers or copolymers, styrene homopolymers or copolymers, partly crosslinked products of these homopolymers or copolymers, refractory oxides or refractory composite oxides of a Group IIA, IIIA, IVA or IVB metal in the Periodic Table of Elements, clay, molecular sieve, mica, montmorillonite, bentonite and kieselguhr, preferably one or more selected from the group consisting of partly crosslinked styrene polymers, silica, alumina, magnesia, silica-alumina, magnesia-alumina, titanium oxide, molecular sieve and montmorillonite, more preferably silica, and/or the magnesium compound is one or more selected from the group consisting of a magnesium halide, an alkoxy magnesium halide, an alkoxy magnesium, an alkyl magnesium, an alkyl magnesium halide and an alkyl alkoxy magnesium, preferably one or more selected from the group consisting of a magnesium halide, more preferably magnesium chloride.

5. The process according to any of the aforesaid aspects, wherein the solvent is one or more selected from the group consisting of a C₆₋₁₂ aromatic hydrocarbon, a halogenated C₆₋₁₂ aromatic hydrocarbon, an ester and an ether, preferably one or more selected from the group consisting of a C₆₋₁₂ aromatic hydrocarbon and tetrahydrofuran, more preferably tetrahydrofuran.

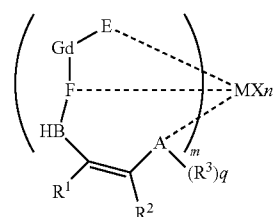
6. The process according to any of the aforesaid aspects, wherein the nonmetallocene complex is one or more selected from the group consisting of the compounds having the following structure,



preferably one or more selected from the group consisting of the following compound (A) and the following compound (B),

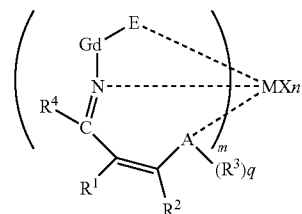


(A)

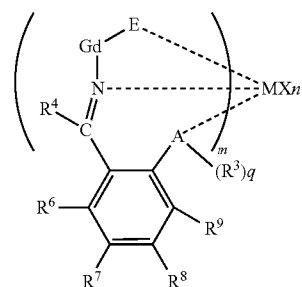


(B)

more preferably one or more selected from the group consisting of the following compound (A-1), the following compound (A-2), the following compound (A-3), the following compound (A-4), the following compound (B-1), the following compound (B-2), the following compound (B-3), and the following compound (B-4),



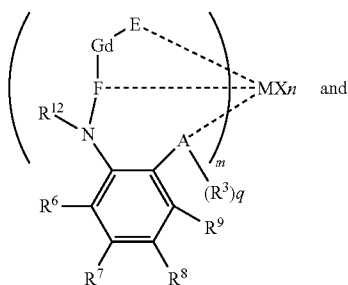
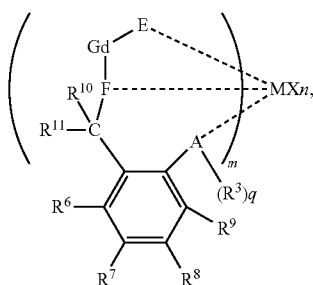
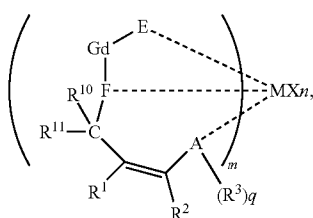
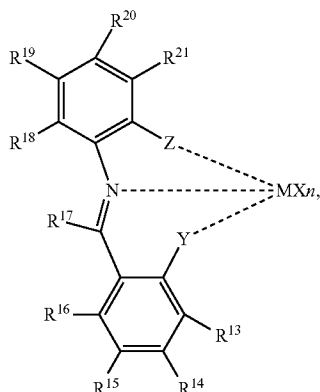
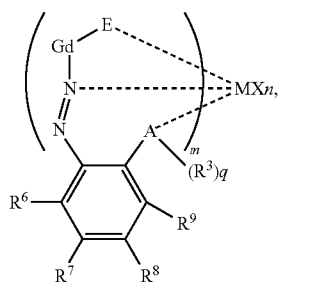
(A-1)



(A-2)

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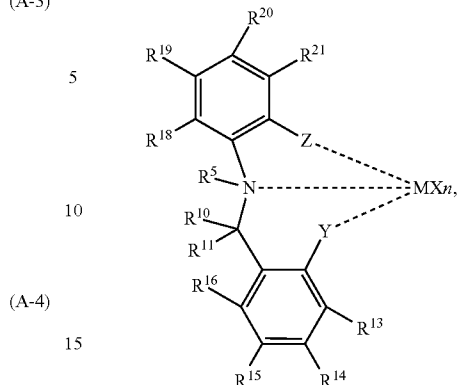


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-continued

(A-3)

(B-4)



(A-4)

in all of the aforesaid formulae,

q is 0 or 1;

d is 0 or 1;

m is 1, 2 or 3;

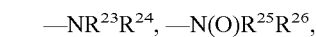
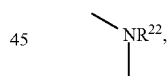
M is selected from the group consisting of a Group III to XI metal atom in the Periodic Table of Elements, preferably from the group consisting of a Group IVB metal atom, more preferably from the group consisting of Ti(IV) and Zr(IV);

n is 1, 2, 3 or 4, depending on the valence of the central metal atom M;

X is selected from the group consisting of a halogen atom, a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl, an oxygen-containing group, a nitrogen-containing group, a sulfur-containing group, a boron-containing group, an aluminium-containing group, a phosphor-containing group, a silicon-containing group, a germanium-containing group, and a tin-containing group, when multiple Xs exist, the Xs may be the same as or different from one another, and may form a bond or a ring with one another;

A is selected from the group consisting of an oxygen atom, a sulfur atom, a selenium atom,

(B-2)



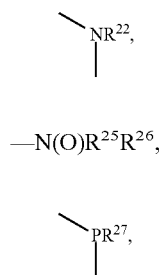
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(B-3)

—PR²⁸R²⁹, —P(O)R³⁰OR³¹, a sulfone group, a sulfoxide group and —Se(O)R³⁹, wherein N, O, S, Se and P each represents a coordination atom;

B is selected from the group consisting of a nitrogen atom, a nitrogen-containing group, a phosphor-containing group and a C₁-C₃₀ hydrocarbyl;

D is selected from the group consisting of a nitrogen atom, an oxygen atom, a sulfur atom, a selenium atom, a phosphor atom, a nitrogen-containing group, a phosphor-containing group, a C₁-C₃₀ hydrocarbyl, a sulfone group, a sulfoxide group,



and $-\text{P}(\text{O})\text{R}^{32}(\text{OR}^{33})$, wherein N, O, S, Se and P each represents a coordination atom;

E is selected from the group consisting of a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group, a phosphor-containing group and a cyano group, wherein N, O, S, Se and P each represents a coordination atom;

F is selected from the group consisting of a nitrogen atom, a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group and a phosphor-containing group, wherein N, O, S, Se and P each represents a coordination atom;

G is selected from the group consisting of a C_1 - C_{30} hydrocarbyl, a substituted C_1 - C_{30} hydrocarbyl and an inert functional group;

Y is selected from the group consisting of an oxygen atom, a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group and a phosphor-containing group, wherein N, O, S, Se and P each represents a coordination atom;

Z is selected from the group consisting of a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group, a phosphor-containing group and a cyano group, wherein N, O, S, Se and P each represents a coordination atom;

$\rightarrow$ represents a single bond or a double bond;

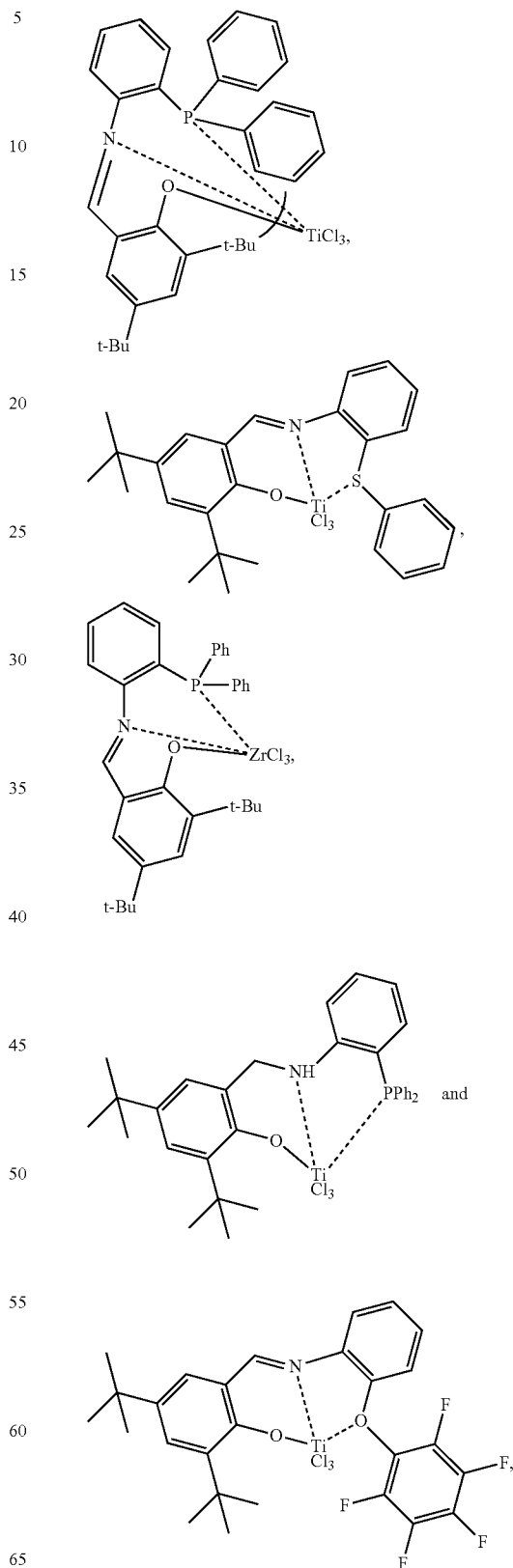
- represents a covalent bond or an ionic bond;

--- represents a coordination bond, a covalent bond or an ionic bond;

R^1 to R^4 , R^6 to R^{36} , R^{38} and R^{39} are each independently selected from the group consisting of a hydrogen atom, a C_1 - C_{30} hydrocarbyl, a substituted C_1 - C_{30} hydrocarbyl and an inert functional group, wherein these groups may be identical to or different from one another, and any adjacent groups may form a bond or a ring (preferably an aromatic ring) with one another; and

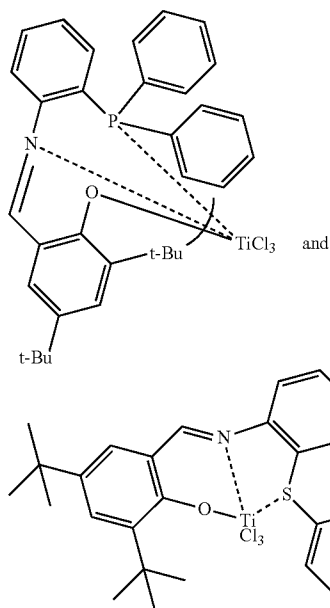
R^5 is selected from the group consisting of the lone pair electron on the nitrogen atom, a hydrogen atom, a C_1 - C_{30} hydrocarbyl, a substituted C_1 - C_{30} hydrocarbyl, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a selenium-containing group, and a phosphor-containing group, with the proviso that when R^5 is the oxygen-containing group, the sulfur-containing group, the nitrogen-containing group, the selenium-containing group or the phosphor-containing group, N, O, S, P and Se in the group R^5 each can act as a coordination atom to coordinate with the central metal atom (the Group IVB metal atom),

more preferably one or more selected from the group consisting of the following compounds,

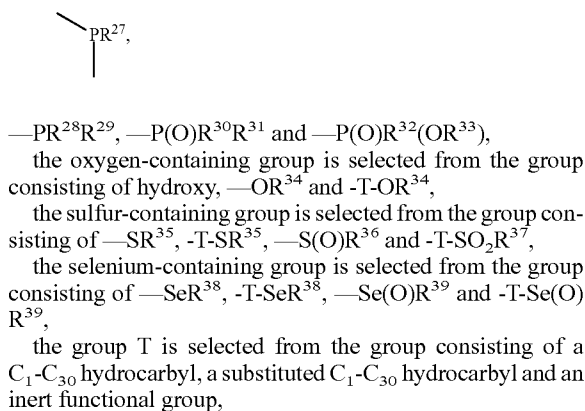
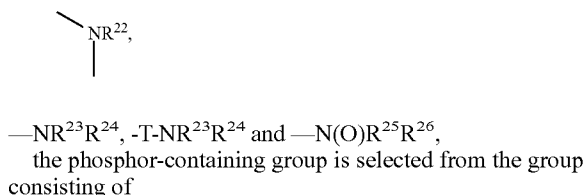


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more preferably one or more selected from the group consisting of the following compounds,



7. The process according to any of the aforesaid aspects, wherein, the halogen atom is selected from the group consisting of F, Cl, Br and I, group is selected from the group consisting of



R³⁷ is selected from the group consisting of a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl and an inert functional group,

the C₁-C₃₀ hydrocarbyl is selected from the group consisting of a C₁-C₃₀ alkyl group, a C₇-C₅₀ alkylaryl group, a C₇-C₅₀ aralkyl group, a C₃-C₃₀ cyclic alkyl group, a C₂-C₃₀ alkenyl group, a C₂-C₃₀ alkynyl group, a C₆-C₃₀ aryl group, a C₈-C₃₀ fused-ring group and a C₄-C₃₀ heterocycle group,

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wherein the heterocycle group contains 1 to 3 hetero atom(s) selected from the group consisting of a nitrogen atom, an oxygen atom and a sulfur atom,

the substituted C₁-C₃₀ hydrocarbyl is selected from the group consisting of the C₁-C₃₀ hydrocarbyl having one or more substituent(s) selected from the halogen atom and the C₁-C₃₀ alkyl group,

the inert functional group is selected from the group consisting of the halogen atom, the oxygen-containing group, the nitrogen-containing group, a silicon-containing group, a germanium-containing group, the sulfur-containing group, a tin-containing group, a C₁-C₁₀ ester group and a nitro group,

the boron-containing group is selected from the group consisting of BF₄⁻, (C₆F₅)₄B⁻ and (R⁴⁰BAr₃)⁻,

the aluminium-containing group is selected from the group consisting of an alkyl aluminium, AlPh₄⁻, AlF₄⁻, AlCl₄⁻, AlBr₄⁻, AlI₄⁻ and R⁴¹AlAr₃,

the silicon-containing group is selected from the group consisting of —SiR⁴²R⁴³R⁴⁴, and —T-SiR⁴⁵,

the germanium-containing group is selected from the group consisting of —GeR⁴⁶R⁴⁷R⁴⁸, and —T-GeR⁴⁹,

the tin-containing group is selected from the group consisting of —SnR⁵⁰R⁵¹R⁵², —T-SnR⁵³ and —T-Sn(O)R⁵⁴,

the Ar group represents a C₆-C₃₀ aryl group,

R⁴⁰ to R⁵⁴ are each independently selected from the group consisting of a hydrogen atom, the C₁-C₃₀ hydrocarbyl, the substituted C₁-C₃₀ hydrocarbyl and the inert functional group, wherein these groups may be identical to or different from one another, and any adjacent groups may form a bond or a ring with one another, and

the group T is defined as aforesaid.

8. The process according to any of the aforesaid aspects, wherein ratio by molar of the magnesium compound (based on Mg) to the nonmetallocene complex is 1:0.01-1, preferably 1:0.04-0.4, more preferably 1:0.08-0.2, ratio of the magnesium compound to the solvent is 1 mol:75~400 ml, preferably 1 mol:150~300 ml, more preferably 1 mol:200~250 ml, ratio by weight of the magnesium compound (on a solid basis) to the porous carrier is 1:0.1-20, preferably 1:0.5-10, more preferably 1:1-5, and ratio by volume of the precipitating agent to the solvent is 1:0.2~5, preferably 1:0.5~2, more preferably 1:0.8~1.5.

9. The process according to any of the aforesaid aspects, wherein ratio by molar of the magnesium compound (based on Mg) to the nonmetallocene complex is 1:0.01-1, preferably 1:0.04-0.4, more preferably 1:0.08-0.2, ratio of the magnesium compound to the solvent is 1 mol:75~400 ml, preferably 1 mol:150~300 ml, more preferably 1 mol:200~250 ml, ratio by weight of the magnesium compound (on a solid basis) to the porous carrier is 1:0.1-20, preferably 1:0.5-10, more preferably 1:1-5, ratio by volume of the precipitating agent to the solvent is 1:0.2~5, preferably 1:0.5~2, more preferably 1:0.8~1.5, and ratio by molar of the magnesium compound (based on Mg) to the chemical treating agent (based on the Group IVB metal) is 1:0.01-1, preferably 1:0.01-0.50, more preferably 1:0.10-0.30.

10. The process according to any of the aforesaid aspects, wherein the precipitating agent is one or more selected from the group consisting of an alkane, a cyclic alkane, a halogenated alkane and a halogenated cyclic alkane, preferably one or more selected from the group consisting of pentane, hexane, heptane, octane, nonane, decane, cyclohexane, cyclopentane, cycloheptane, cyclodecane, cyclononane, dichloromethane, dichloro hexane, dichloro heptane, trichloromethane, trichloro ethane, trichloro butane, dibromo methane, dibromo ethane, dibromo heptane, tribromo methane, tribromo ethane, tribromo butane, chlorinated cyclopentane,

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chlorinated cyclohexane, chlorinated cycloheptane, chlorinated cyclooctane, chlorinated cyclononane, chlorinated cyclodecane, brominated cyclopentane, brominated cyclohexane, brominated cycloheptane, brominated cyclooctane, brominated cyclononane and brominated cyclodecane, more preferably one or more selected from the group consisting of hexane, heptane, decane and cyclohexane, most preferably hexane.

11. The process according to any of the aforesaid aspects, wherein the Group IVB metal compound is one or more selected from the group consisting of a Group IVB metal halide, a Group IVB metal alkylate, a Group IVB metal alkoxylate, a Group IVB metal alkyl halide, and a Group IVB metal alkoxy halide, preferably one or more selected from the group consisting of a Group IVB metal halide, more preferably one or more selected from the group consisting of TiCl_4 , TiBr_4 , ZrCl_4 , ZrBr_4 , HfCl_4 and HfBr_4 , more preferably one or more selected from the group consisting of TiCl_4 and ZrCl_4 .

12. The process according to any of the aforesaid aspects, wherein the aluminoxane is one or more selected from the group consisting of methyl aluminoxane, ethyl aluminoxane, isobutyl aluminoxane and n-butyl aluminoxane, preferably one or more selected from the group consisting of methyl aluminoxane and isobutyl aluminoxane, and the alkylaluminum is one or more selected from the group consisting of trimethyl aluminum, triethyl aluminum, tripropyl aluminum, triisobutyl aluminum, tri-n-butyl aluminum, triisoamyl aluminum, tri-n-amy aluminum, trihexyl aluminum, tri-isohexyl aluminum, diethyl methyl aluminum and ethyl dimethyl aluminum, more preferably one or more selected from the group consisting of trimethyl aluminum, triethyl aluminum, tripropyl aluminum and triisobutyl aluminum, most preferably one or more selected from the group consisting of triethyl aluminum and triisobutyl aluminum.

13. The process according to any of the aforesaid aspects, wherein ratio by molar of the magnesium compound (based on Mg) to the assistant chemical treating agent (based on Al) is 1:0-1.0, preferably 1:0-0.5, more preferably 1:0.1-0.5.

14. A supported nonmetallocene catalyst, produced in line with the process according to any of the aspects 1 to 13.

15. An olefin homopolymerization/copolymerization process, wherein the supported nonmetallocene catalyst according to the aspect 14 is used as the main catalyst, in combination of one or more selected from the group consisting of an aluminoxane, an alkylaluminum, a halogenated alkyl aluminum, a fluoroborane, an alkylboron and an alkylboron ammonium salt as the co-catalyst, for homopolymerization or copolymerization of the olefin.

16. An olefin homopolymerization/copolymerization process, comprising the steps of: producing a supported nonmetallocene catalyst in line with the process according to any of the aspects 1 to 13; and using the supported nonmetallocene catalyst as the main catalyst, in combination of one or more selected from the group consisting of an aluminoxane, an alkylaluminum, a halogenated alkyl aluminum, a fluoroborane, an alkylboron and an alkylboron ammonium salt as the co-catalyst, for homopolymerization or copolymerization of the olefin.

Effect of the Invention

According to the first and second embodiments of this invention, the following effects can be obtained.

The process for producing the supported nonmetallocene catalyst according to this invention is simple and feasible. It is easy, to adjust the load of the nonmetallocene complex, and it

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is possible for it to perform sufficiently in catalyzing olefin polymerization to obtain an olefin polymer product.

According to the process of this invention (concerning the first embodiment), the catalyst has been produced by directly drying the slurry, and therefore it is easy to adjust the composition and amount of the essential materials in the catalyst.

According to the process of this invention (concerning the second embodiment), the catalyst has been produced by sufficiently precipitating the slurry in the presence of a precipitating agent and then filtering, washing and drying same, and therefore the bonding between the essential materials in the catalyst is relatively strong.

When a catalyst system is constituted by using the catalyst according to this invention in combination with a co-catalyst, the polymer resulted from olefin polymerization exhibits a narrowed molecular weight distribution, when used for copolymerization, the catalyst system shows a significant co-monomer effect, i.e. under relatively the same conditions, the activity in copolymerization is higher than that in homopolymerization.

According to the third and fourth embodiments of this invention, the following effects can be obtained.

The process for producing the supported nonmetallocene catalyst according to this invention is simple and feasible, and it is easy to control the composition and amount of the essential materials in the catalyst. Further, it is easy to adjust the load of the nonmetallocene complex, and it is possible for it to perform sufficiently in catalyzing olefin polymerization to obtain an olefin polymer product. Still further, it is possible to adjust the molecular weight distribution and the viscosity averaged molecular weight of the polymer product (for example, the ultra high molecular weight polyethylene) by altering the amount of the nonmetallocene complex to be introduced.

Further, by altering the amount of the assistant chemical treating agent and that of the chemical treating agent to be introduced, it is possible to obtain a supported nonmetallocene catalyst showing a easily controllable polymerization activity, from low to high, whereby responding to different olefin polymerization requirements, and it is possible to adjust the performances of the catalyst and that of the polymer in combination of the step of altering the amount of the nonmetallocene complex to be introduced.

According to the process of this invention (concerning the fourth embodiment), the composite carrier has been produced by sufficiently precipitating the slurry in the presence of a precipitating agent and then filtering, washing and drying same, and therefore the bonding between the essential materials in the catalyst is relatively strong.

The active components (i.e. the nonmetallocene complex and the chemical treating agent) in the supported nonmetallocene catalyst produced in line with the process according to this invention show a synergic effect, i.e. the activity obtained with the case when both components exist is higher than that when only either component exists.

Further discovered is that, when a catalyst system is constituted by using the catalyst according to this invention in combination with a co-catalyst, only a comparatively small amount of the co-catalyst (for example, methyl aluminoxane or triethyl aluminum) is needed to achieve a comparatively high polymerization activity, and when used for copolymerization, the catalyst system shows a significant co-monomer effect, i.e. under relatively the same conditions, the activity in copolymerization is higher than that in homopolymerization. Further, the polymer (for example polyethylene) resulted

from olefin homopolymerization or copolymerization has a desirable polymer morphology and a high polymer bulk density.

DETAILED DESCRIPTION OF THE INVENTION

This invention will be described in details hereinafter with reference to the following specific embodiments. However, it is known that the protection scope of this invention should not be construed as limited to these specific embodiments, but rather determined by the attached claims.

According to this invention, generally disclosed are the following first to fourth embodiments.

The first embodiment relates to a process for producing a supported nonmetallocene catalyst, which comprises the steps of: dissolving a magnesium compound and a nonmetallocene complex in a solvent, to obtain a magnesium compound solution; mixing a porous carrier or a thermally activated porous carrier with the magnesium compound solution to obtain a slurry; and drying the slurry to obtain the supported nonmetallocene catalyst.

The second embodiment relates to a process for producing a supported nonmetallocene catalyst, which comprises the steps of: dissolving a magnesium compound and a nonmetallocene complex in a solvent, to obtain a magnesium compound solution; mixing a porous carrier or a thermally activated porous carrier with the magnesium compound solution to obtain a slurry; and introducing into the slurry a precipitating agent to obtain the supported nonmetallocene catalyst.

The third embodiment relates to a process for producing a supported nonmetallocene catalyst, which comprises the steps of: dissolving a magnesium compound and a nonmetallocene complex in a solvent, to obtain a magnesium compound solution; mixing a porous carrier or a thermally activated porous carrier with the magnesium compound solution to obtain a slurry; drying the slurry to obtain a composite carrier; and treating the composite carrier with a chemical treating agent selected from the group consisting of Group IVB metal compounds to obtain the supported nonmetallocene catalyst.

The fourth embodiment relates to a process for producing a supported nonmetallocene catalyst, which comprises the steps of: dissolving a magnesium compound and a nonmetallocene complex in a solvent, to obtain a magnesium compound solution; mixing a porous carrier or a thermally activated porous carrier with the magnesium compound solution to obtain a slurry; introducing into the slurry a precipitating agent to obtain a composite carrier; and treating the composite carrier with a chemical treating agent selected from the group consisting of Group IVB metal compounds to obtain the supported nonmetallocene catalyst.

First of all, the step of obtaining the magnesium compound solution according to the first to fourth embodiments of this invention is detailedly described as follows.

Specifically, the magnesium compound (solid) and the nonmetallocene complex are dissolved in a suitable solvent (hereinafter referred to as a solvent for dissolving the magnesium compound) to obtain the magnesium compound solution.

As the solvent, a C_{6-12} aromatic hydrocarbon, a halogenated C_{6-12} aromatic hydrocarbon, an ester and an ether can be exemplified. Specifically, toluene, xylene, trimethyl benzene, ethyl benzene, diethyl benzene, chlorinated toluene, chlorinated ethyl benzene, brominated toluene, brominated ethyl benzene, ethyl acetate and tetrahydrofuran can be exemplified. Preference is given to the C_{6-12} aromatic hydrocarbon or tetrahydrofuran, more preferably tetrahydrofuran.

The solvents could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

For preparation of the magnesium compound solution, the magnesium compound and the nonmetallocene complex are metered into and dissolved in said solvent.

During preparation of the magnesium compound solution, it is desirable that the ratio of the magnesium compound (based on Mg and on a solid basis) to the solvent for dissolving the magnesium compound is generally 1 mol:75~400 ml, preferably 1 mol:150~300 ml, more preferably 1 mol:200~250 ml.

According to this invention, as the amount of the nonmetallocene complex to be used, it is desirable that the ratio by molar of the magnesium compound (based on Mg and on a solid basis) to the nonmetallocene complex is 1:0.01-1, preferably 1:0.04-0.4, more preferably 1:0.08-0.2.

The duration for preparing the magnesium compound solution (i.e. the duration for dissolving the magnesium compound and the nonmetallocene complex) is not specifically limited, usually 0.5 to 24 hours, preferably 4 to 24 hours. During preparation of the magnesium compound solution, any stirring means for example, a stirring paddle (whose rotational speed could be 10 to 1000 r/min), could be used to facilitate dissolution of the magnesium compound and the nonmetallocene complex. If needed, heat can be suitably applied to facilitate the dissolution.

The magnesium compound is further described as follows.

According to this invention, the term "magnesium compound" is explained in a normal sense as known in this field, and refers to an organic or inorganic solid anhydrous Mg-containing compound conventionally used as a carrier for a supported catalyst for olefin polymerization.

According to this invention, as the magnesium compound, a magnesium halide, an alkoxy magnesium halide, an alkoxy magnesium, an alkyl magnesium, an alkyl magnesium halide and an alkyl alkoxy magnesium can be exemplified.

Specifically, the magnesium halide for example, could be selected from the group consisting of magnesium chloride ($MgCl_2$), magnesium bromide ($MgBr_2$), magnesium iodide (MgI_2) and magnesium fluoride (MgF_2), etc., such as magnesium chloride.

The alkoxy magnesium halide for example, could be selected from the group consisting of methoxy magnesium chloride ($Mg(OCH_3)Cl$), ethoxy magnesium chloride ($Mg(OC_2H_5)Cl$), propoxy magnesium chloride ($Mg(OC_3H_7)Cl$), n-butoxy magnesium chloride ($Mg(OC_4H_9)Cl$), isobutoxy magnesium chloride ($Mg(i-OC_4H_9)Cl$), methoxy magnesium bromide ($Mg(OCH_3)Br$), ethoxy magnesium bromide ($Mg(OC_2H_5)Br$), propoxy magnesium bromide ($Mg(OC_3H_7)Br$), n-butoxy magnesium bromide ($Mg(OC_4H_9)Br$), isobutoxy magnesium bromide ($Mg(i-OC_4H_9)Br$), methoxy magnesium iodide ($Mg(OCH_3)I$), ethoxy magnesium iodide ($Mg(OC_2H_5)I$), propoxy magnesium iodide ($Mg(OC_3H_7)I$), n-butoxy magnesium iodide ($Mg(OC_4H_9)I$) and isobutoxy magnesium iodide ($Mg(i-OC_4H_9)I$), etc., such as methoxy magnesium chloride, ethoxy magnesium chloride and isobutoxy magnesium chloride.

The alkoxy magnesium for example, could be selected from the group consisting of methoxy magnesium ($Mg(OCH_3)_2$), ethoxy magnesium ($Mg(OC_2H_5)_2$), propoxy magnesium ($Mg(OC_3H_7)_2$), butoxy magnesium ($Mg(OC_4H_9)_2$), isobutoxy magnesium ($Mg(i-OC_4H_9)_2$) and 2-ethyl hexyloxy magnesium ($Mg(OCH_2CH(C_2H_5)C_4H_9)_2$), etc., such as ethoxy magnesium and isobutoxy magnesium.

The alkyl magnesium for example, could be selected from the group consisting of methyl magnesium ($Mg(CH_3)_2$), ethyl magnesium ($Mg(C_2H_5)_2$), propyl magnesium (Mg

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(C₃H₇)₂), n-butyl magnesium (Mg(C₄H₉)₂) and isobutyl magnesium (Mg(i-C₄H₉)₂), etc., such as ethyl magnesium and n-butyl magnesium.

The alkyl magnesium halide for example, could be selected from the group consisting of methyl magnesium chloride (Mg(CH₃)Cl), ethyl magnesium chloride (Mg(C₂H₅)Cl), propyl magnesium chloride (Mg(C₃H₇)Cl), n-butyl magnesium chloride (Mg(C₄H₉)Cl), isobutyl magnesium chloride (Mg(i-C₄H₉)Cl), methyl magnesium bromide (Mg(CH₃)Br), ethyl magnesium bromide (Mg(C₂H₅)Br), propyl magnesium bromide (Mg(C₃H₇)Br), n-butyl magnesium bromide (Mg(C₄H₉)Br), isobutyl magnesium bromide (Mg(i-C₄H₉)Br), methyl magnesium iodide (Mg(CH₃)I), ethyl magnesium iodide (Mg(C₂H₅)I), propyl magnesium iodide (Mg(C₃H₇)I), n-butyl magnesium iodide (Mg(C₄H₉)I) and isobutyl magnesium iodide (Mg(i-C₄H₉)I), etc., such as methyl magnesium chloride, ethyl magnesium chloride and isobutyl magnesium chloride.

The alkyl alkoxy magnesium for example, could be selected from the group consisting of methyl methoxy magnesium (Mg(OCH₃)(CH₃)), methyl ethoxy magnesium (Mg(OC₂H₅)(CH₃)), methyl propoxy magnesium (Mg(OC₃H₇)(CH₃)), methyl n-butoxy magnesium (Mg(OC₄H₉)(CH₃)), methyl isobutoxy magnesium (Mg(i-OC₄H₉)(CH₃)), ethyl methoxy magnesium (Mg(OCH₃)(C₂H₅)), ethyl ethoxy magnesium (Mg(OC₂H₅)(C₂H₅)), ethyl propoxy magnesium (Mg(OC₃H₇)(C₂H₅)), ethyl n-butoxy magnesium (Mg(OC₄H₉)(C₂H₅)), ethyl isobutoxy magnesium (Mg(i-OC₄H₉)(C₂H₅)), propyl methoxy magnesium (Mg(OCH₃)(C₃H₇)), propyl ethoxy magnesium (Mg(OC₂H₅)(C₃H₇)), propyl propoxy magnesium (Mg(OC₃H₇)(C₃H₇)), propyl n-butoxy magnesium (Mg(OC₄H₉)(C₃H₇)), propyl isobutoxy magnesium (Mg(i-OC₄H₉)(C₃H₇)), n-butyl methoxy magnesium (Mg(OCH₃)(C₄H₉)), n-butyl ethoxy magnesium (Mg(OC₂H₅)(C₄H₉)), n-butyl propoxy magnesium (Mg(OC₃H₇)(C₄H₉)), n-butyl n-butoxy magnesium (Mg(OC₄H₉)(C₄H₉)), n-butyl isobutoxy magnesium (Mg(i-OC₄H₉)(C₄H₉)), isobutyl methoxy magnesium (Mg(OCH₃)(i-C₄H₉)), isobutyl ethoxy magnesium (Mg(OC₂H₅)(i-C₄H₉)), isobutyl propoxy magnesium (Mg(OC₃H₇)(i-C₄H₉)), isobutyl n-butoxy magnesium (Mg(OC₄H₉)(i-C₄H₉)) and isobutyl isobutoxy magnesium (Mg(i-OC₄H₉)(i-C₄H₉)), etc., such as butyl ethoxy magnesium.

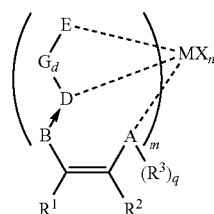
The magnesium compounds could be used with one kind or as a mixture of two or more kinds, but without any limitation thereto.

For example, if more than one magnesium compounds are used as a mixture, the ratio by molar of one magnesium compound to another magnesium compound in the mixture could be, for example, 0.25 to 4:1, such as 0.5 to 3:1, such as 1 to 2:1.

According to this invention, the term "nonmetallocene complex" refers to an organic metallic compound capable of exhibiting a catalysis activity in olefin polymerization when combined with an aluminoxane (sometimes hereinafter referred to as a nonmetallocene complex for olefin polymerization). The compound contains a central metal atom and at least one multi-dentate ligand (preferably a tri or more-dentate ligand) bonding to the central metal atom by a coordination bond. The term "nonmetallocene ligand" corresponds to the multi-dentate ligand.

According to this invention, the nonmetallocene complex is selected from the compounds having the following structure,

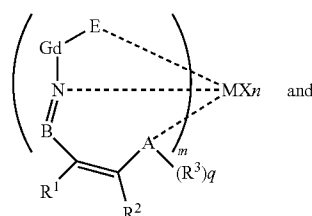
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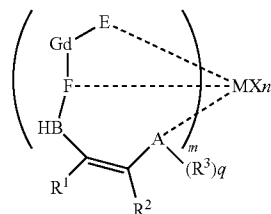
According to aforesaid chemical formula, the ligands which form a coordination bond with the central metal atom M contain n of the groups X and m of the multi-dentate ligands (the structure in the parenthesis). According to the chemical formula of said multi-dentate ligand, the groups A, D and E (the coordination groups) form a coordination bond with the central metal atom M through the coordination atoms (for example, hetero atoms like N, O, S, Se and P) contained in these groups.

According to this invention, the absolute value of the total sum of the negative charges carried by all of the ligands (including the group X and the multi-dentate ligand) is equal to that of the positive charges carried by the central metal atom M.

According to a further embodiment of this invention, the nonmetallocene complex is selected from the following compound (A) and the following compound (B),

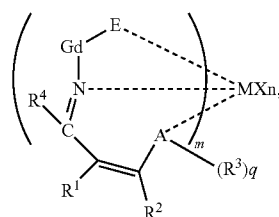


(A)



(B)

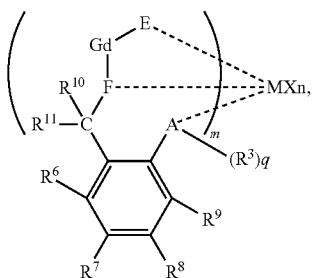
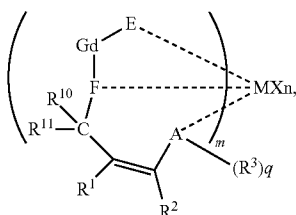
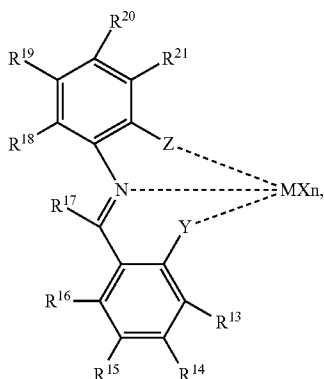
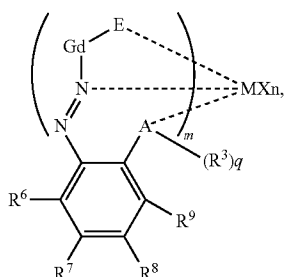
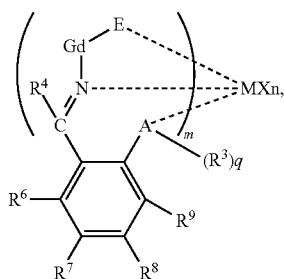
According to a further embodiment of this invention, the nonmetallocene complex is selected from the following compound (A-1), the following compound (A-2), the following compound (A-3), the following compound (A-4), the following compound (B-1), the following compound (B-2), the following compound (B-3), and the following compound (B-4),



(A-1)

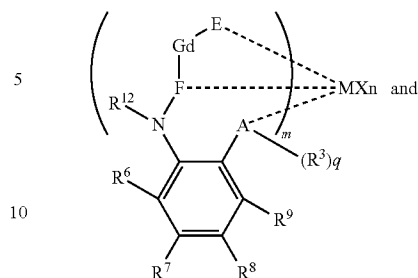
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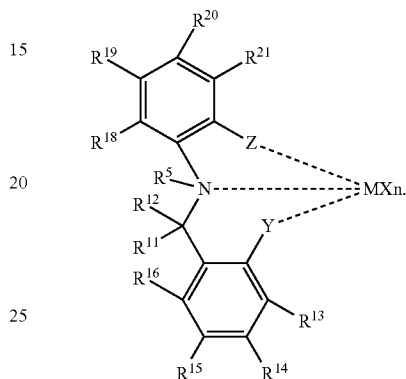
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(A-2)



(B-3)

(A-3)



(B-4)

(A-4)

In all of the aforesaid formulae,

q is 0 or 1;

d is 0 or 1;

m is 1, 2 or 3;

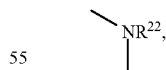
M is selected from the group consisting of a Group III to XI metal atom in the Periodic Table of Elements, preferably a Group IVB metal atom, for example, Ti(IV), Zr(IV), Hf(IV), Cr(III), Fe(III), Ni(II), Pd(II) or Co(II);

n is 1, 2, 3 or 4, depending on the valence of the central metal atom M;

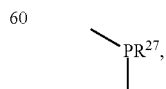
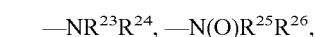
X is selected from the group consisting of a halogen atom, a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl, an oxygen-containing group, a nitrogen-containing group, a sulfur-containing group, a boron-containing group, an aluminium-containing group, a phosphor-containing group, a silicon-containing group, a germanium-containing group, and a tin-containing group, when multiple Xs exist, the Xs may be the same as or different from one another, and may form a bond or a ring with one another;

A is selected from the group consisting of an oxygen atom, a sulfur atom, a selenium atom,

(B-1)



(B-2)

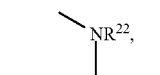


—PR²⁸R²⁹, —P(O)R³⁰OR³¹, a sulfone group, a sulfoxide group and —Se(O)R³⁹, wherein N, O, S, Se and P each represents a coordination atom;

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B is selected from the group consisting of a nitrogen atom, a nitrogen-containing group, a phosphor-containing group and a C₁-C₃₀ hydrocarbyl;

D is selected from the group consisting of a nitrogen atom, an oxygen atom, a sulfur atom, a selenium atom, a phosphor atom, a nitrogen-containing group, a phosphor-containing group, a C₁-C₃₀ hydrocarbyl, a sulfone group, a sulfoxide group,



and $\text{---P(O)R}^{32}(\text{OR}^{33})$, wherein N, O, S, Se and P each represents a coordination atom;

E is selected from the group consisting of a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group, a phosphor-containing group and a cyano group (---CN), wherein N, O, S, Se and P each represents a coordination atom;

F is selected from the group consisting of a nitrogen atom, a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group and a phosphor-containing group, wherein N, O, S, Se and P each represents a coordination atom;

G is selected from the group consisting of a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl and an inert functional group;

Y is selected from the group consisting of an oxygen atom, a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group and a phosphor-containing group, wherein N, O, S, Se and P each represents a coordination atom;

Z is selected from the group consisting of a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group, a phosphor-containing group and a cyano group (---CN), for example, $\text{---NR}^{23}\text{R}^{24}$, $\text{---N(O)R}^{25}\text{R}^{26}$, $\text{---PR}^{28}\text{R}^{29}$, $\text{---P(O)R}^{30}\text{R}^{31}$, ---OR^{34} , ---SR^{35} , ---S(O)R^{36} , ---SeR^{38} or ---Se(O)R^{39} , wherein N, O, S, Se and P each represents a coordination atom;

→ represents a single bond or a double bond;

- represents a covalent bond or an ionic bond;

--- represents a coordination bond, a covalent bond or an ionic bond;

R¹ to R⁴, R⁶ to R³⁶, R³⁸ and R³⁹ are each independently selected from the group consisting of a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl (preferably a halogenated hydrocarbyl, for example $\text{---CH}_2\text{Cl}$ and $\text{---CH}_2\text{CH}_2\text{Cl}$) and an inert functional group, wherein these groups may be identical to or different from one another, and any adjacent groups (for example R¹ and R², R⁶ and R⁷, R⁷ and R⁸, R⁸ and R⁹, R¹³ and R¹⁴, R¹⁴ and R¹⁵, R¹⁵ and R¹⁶, R¹⁸ and R¹⁹, R¹⁹ and R²⁰, R²⁰ and R²¹, R²³ and R²⁴, or R²⁵ and R²⁶) may form a bond or a ring (preferably an aromatic ring, for example a unsubstituted benzene ring or a benzene ring substituted by one to four of a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl (preferably a halogenated hydro-

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carbyl, for example $\text{---CH}_2\text{Cl}$ and $\text{---CH}_2\text{CH}_2\text{Cl}$) or an inert functional group) with one another; and

R⁵ is selected from the group consisting of the lone pair electron on the nitrogen atom, a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a selenium-containing group, and a phosphor-containing group, with the proviso that when R⁵ is the oxygen-containing group, the sulfur-containing group, the nitrogen-containing group, the selenium-containing group or the phosphor-containing group, N, O, S, P and Se in the group R⁵ each can act as a coordination atom to coordinate with the central metal atom (the Group IVB metal atom).

According to this invention, in all of the aforesaid formulae, if necessary, any two or more adjacent groups (for example R²¹ and the group Z, or R¹³ and the group Y) may form a ring with one another, preferably a C₆-C₃₀ aromatic heteroatomic ring containing the hetero atom originated from the group Z or Y, for example a pyridine ring, wherein the aromatic heteroatomic ring is optionally substituted by one or more substituent(s) selected from the group consisting of a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl and an inert functional group.

In the context of this invention, the halogen atom is selected from the group consisting of F, Cl, Br and I, the nitrogen-containing group is selected from the group consisting of



$\text{---NR}^{23}\text{R}^{24}$, $\text{---T-NR}^{23}\text{R}^{24}$ and $\text{---N(O)R}^{25}\text{R}^{26}$, the phosphor-containing group is selected from the group consisting of



$\text{---PR}^{28}\text{R}^{29}$, $\text{---P(O)R}^{30}\text{R}^{31}$ and $\text{---P(O)R}^{32}(\text{OR}^{33})$, the oxygen-containing group is selected from the group consisting of hydroxy, ---OR^{34} and ---T-OR^{34} , the sulfur-containing group is selected from the group consisting of ---SR^{35} , ---T-SR^{35} , ---S(O)R^{36} and $\text{---T-SO}_2\text{R}^{37}$, the selenium-containing group is selected from the group consisting of ---SeR^{38} , ---T-SeR^{38} , ---Se(O)R^{39} and ---T-Se(O)R^{39} , the group T is selected from the group consisting of a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl and an inert functional group, and R³⁷ is selected from the group consisting of a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl and an inert functional group.

In the context of this invention, the C₁-C₃₀ hydrocarbyl is selected from the group consisting of a C₁-C₃₀ alkyl group (for example a C₁-C₆ alkyl group, for example isobutyl group), a C₇-C₅₀ alkylaryl group (for example tolyl, xylyl, diisobutyl phenyl), a C₇-C₅₀ aralkyl group (for example benzyl), a C₃-C₃₀ cyclic alkyl group, a C₂-C₃₀ alkenyl group, a C₂-C₃₀ alkynyl group, a C₆-C₃₀ aryl group (for example phenyl, naphthyl, anthracyl), a C₈-C₃₀ fused-ring group and a C₄-C₃₀ heterocyclic group, wherein the heterocyclic group contains 1 to 3 hetero atom(s) selected from the group consisting of a nitrogen atom, an oxygen atom and a sulfur atom, including for example a pyridyl group, a pyrrolyl group, a furanyl group and a thienyl group.

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In the context of this invention, depending on the nature of the relevant groups to which the C_1 - C_{30} hydrocarbyl bond, it is obvious to a person skilled in the art that the C_1 - C_{30} hydrocarbyl may intend a C_1 - C_{30} hydrocarbon-diyl (a bivalent group, or referred to as a C_1 - C_{30} hydrocarbylene group) or a C_1 - C_{30} hydrocarbon-triyl (a trivalent group).

In the context of this invention, the substituted C_1 - C_{30} hydrocarbyl intends the aforesaid C_1 - C_{30} hydrocarbyl having one or more inert substituent(s). By inert, it means that these inert substituents will not substantially interfere with the coordination process between the aforesaid coordination groups (i.e. the aforesaid groups A, D, E, F, Y and Z, or further, if applicable, the group R^5) and the central metal atom M. In other words, restricted by the specific chemical structure of the present multi-dentate ligand, these substituents are incapable of or have no chance (due to for example steric hindrance) to coordinate with the central metal atom M to form a coordination bond therewith. Generally, the inert substituent refers to the aforesaid halogen atom or C_1 - C_{30} alkyl group (for example a C_1 - C_6 alkyl group, for example isobutyl group).

In the context of this invention, the term "inert functional group" does not comprise the aforesaid C_1 - C_{30} hydrocarbyl or substituted C_1 - C_{30} hydrocarbyl in its concept. As the inert functional group, the halogen atom, the oxygen-containing group, the nitrogen-containing group, a silicon-containing group, a germanium-containing group, the sulfur-containing group, a tin-containing group, a C_1 - C_{10} ester group or a nitro group ($-\text{NO}_2$) can be exemplified.

In the context of this invention, restricted by the specific structure of the present multi-dentate ligand, the inert functional group is characterized that:

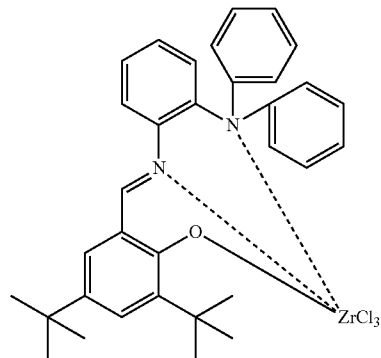
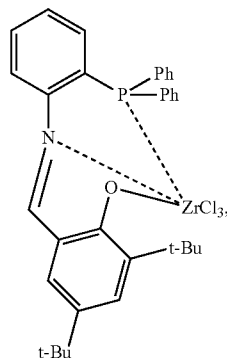
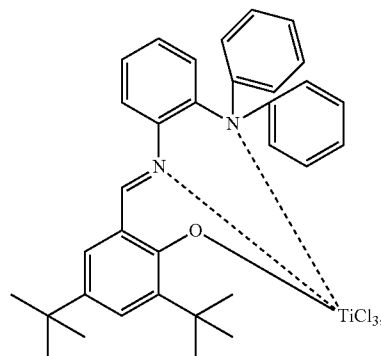
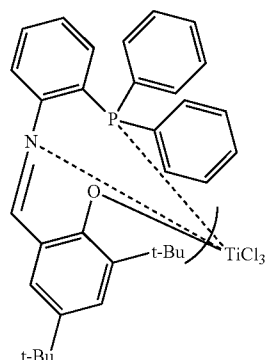
(1) it will not interfere with the coordination process between the aforesaid group A, D, E, F, Y or Z and the central metal atom M, and

(2) its capability to form a coordination bond with the central metal atom M is inferior to the capability of the aforesaid group A, D, E, F, Y or Z to form a coordination bond with the central metal atom M, and will not displace the formed coordination between the central metal atom M and these groups.

In the context of this invention, the boron-containing group is selected from the group consisting of BF_4^- , $(\text{C}_6\text{F}_5)_4\text{B}^-$ and $(\text{R}^{40}\text{BAr}_3)^-$, the aluminium-containing group is selected from the group consisting of an alkyl aluminium, AlPh_4^- , AlF_4^- , AlCl_4^- , AlBr_4^- , AlI_4^- and $\text{R}^{41}\text{AlAr}_3^-$, the silicon-containing group is selected from the group consisting of $-\text{SiR}^{42}\text{R}^{43}\text{R}^{44}$, and $-\text{T-SiR}^{45}$, the germanium-containing group is selected from the group consisting of $-\text{GeR}^{46}\text{R}^{47}\text{R}^{48}$, and $-\text{T-GeR}^{49}$, the tin-containing group is selected from the group consisting of $-\text{SnR}^{50}\text{R}^{51}\text{R}^{52}$, $-\text{T-SnR}^{53}$ and $-\text{T-Sn}(\text{O})\text{R}^{54}$, the Ar group represents a C_6 - C_{30} aryl group, R^{40} to R^{54} are each independently selected from the group consisting of a hydrogen atom, the C_1 - C_{30} hydrocarbyl, the substituted C_1 - C_{30} hydrocarbyl and the inert functional group, wherein these groups may be identical to or different from one another, and any adjacent groups may form a bond or a ring with one another, and the group T is defined as aforesaid.

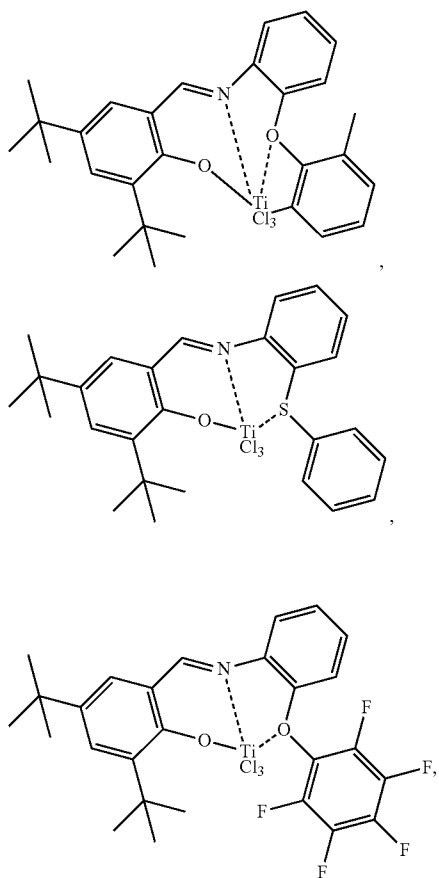
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As the nonmetallocene complex, the following compounds can be further exemplified.

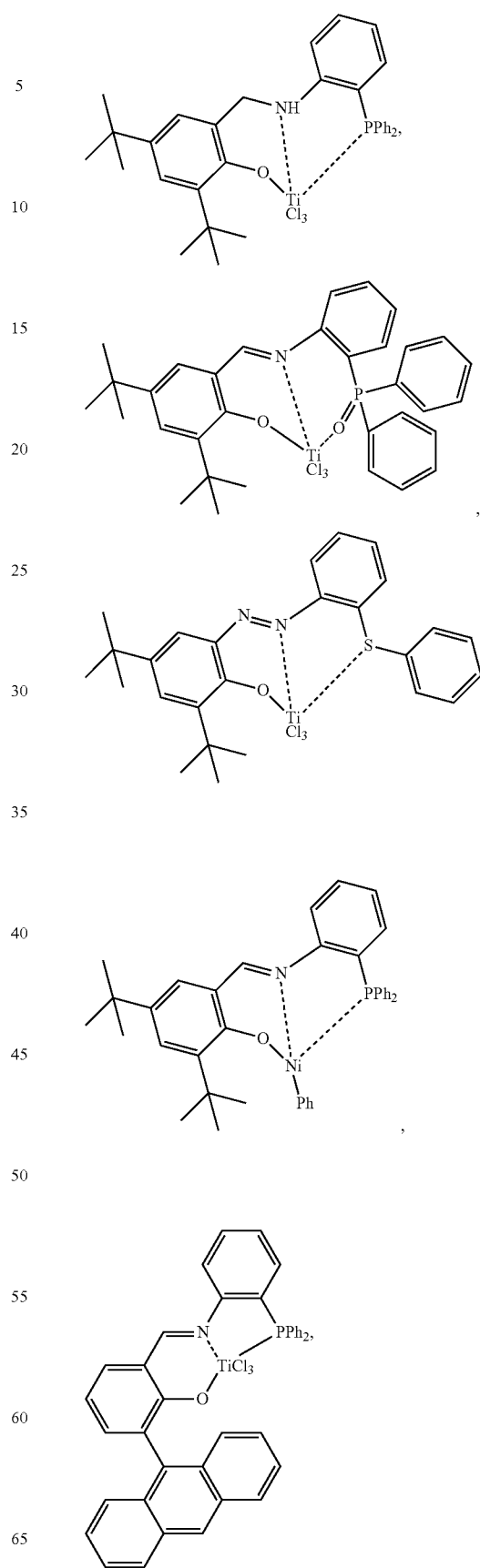


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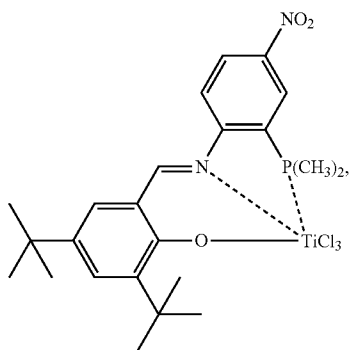
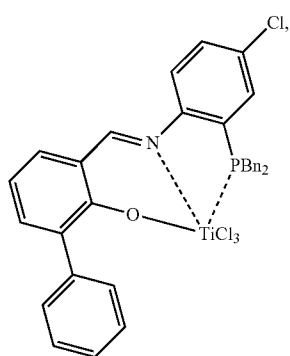
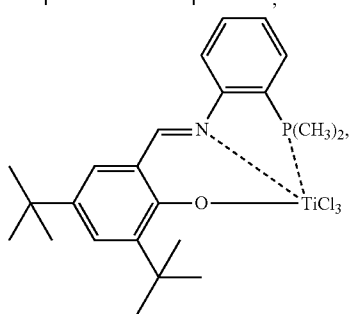
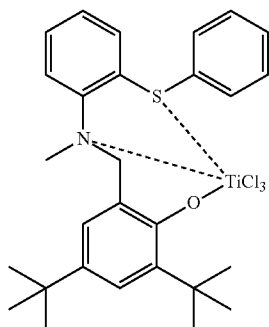
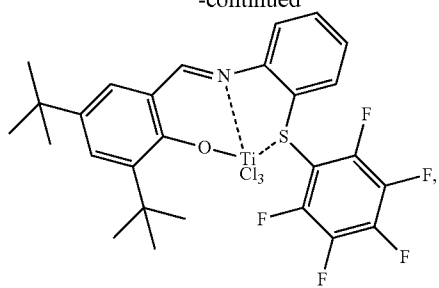
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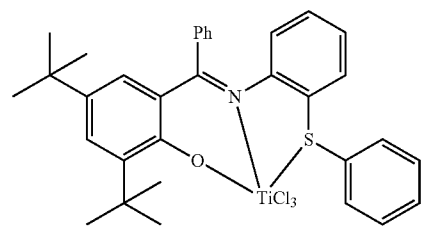
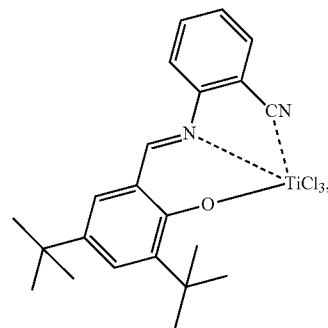
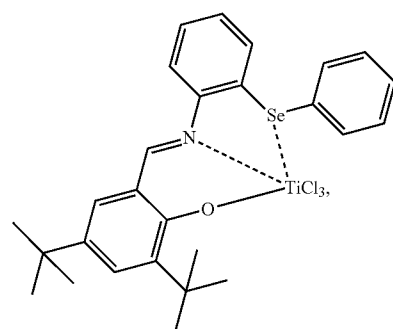
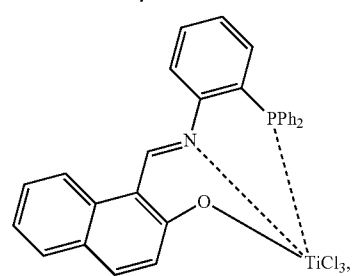
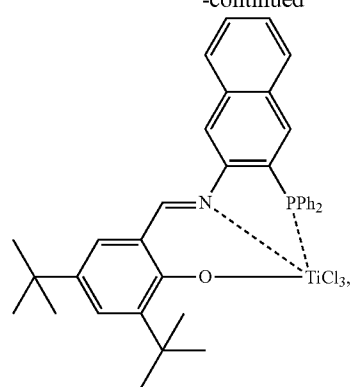
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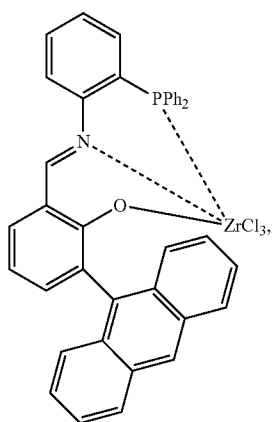
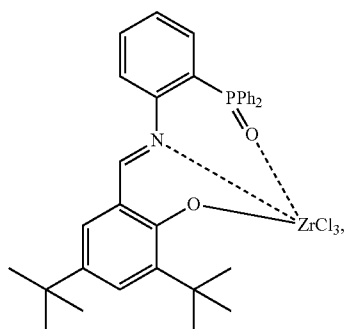
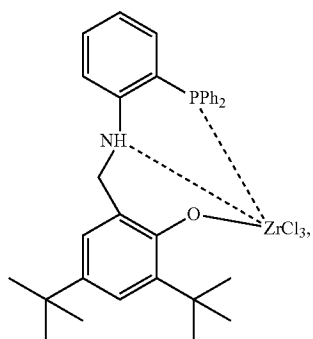
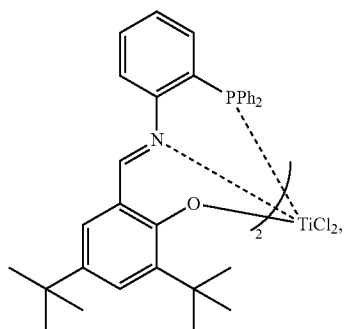
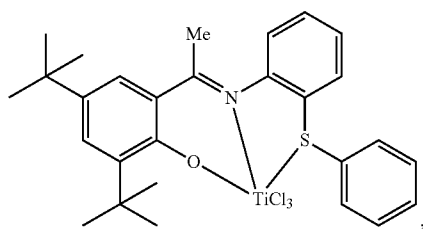
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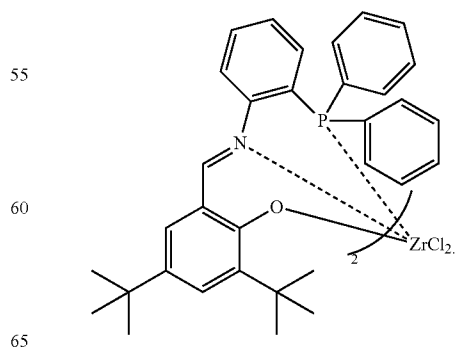
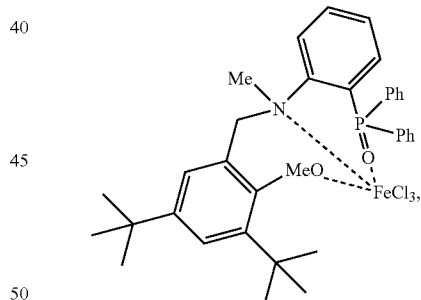
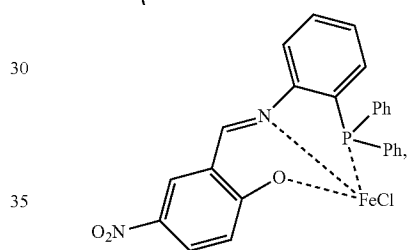
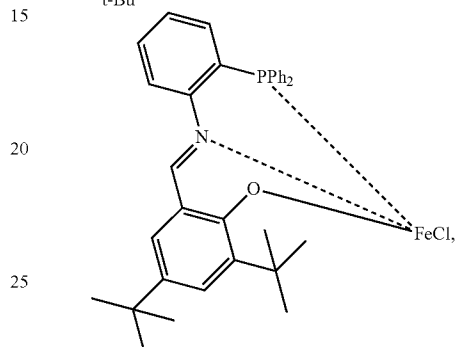
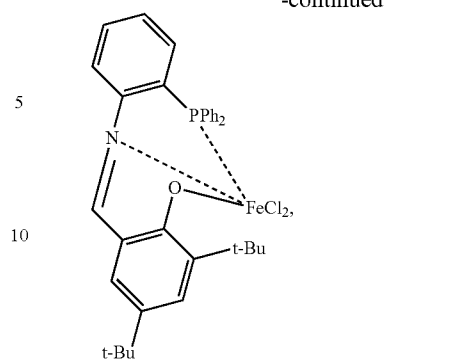


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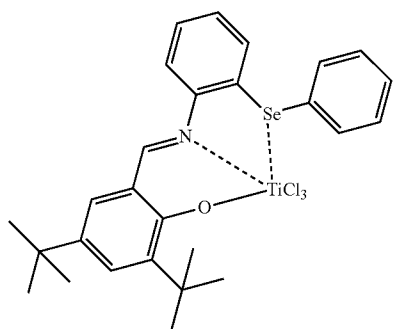
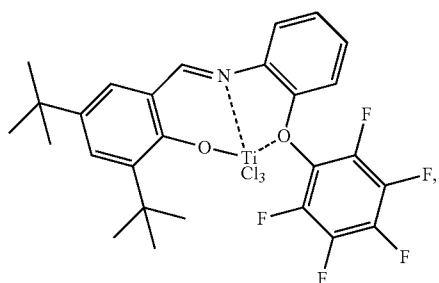
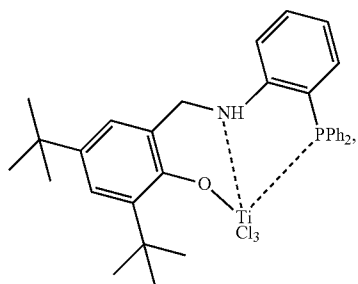
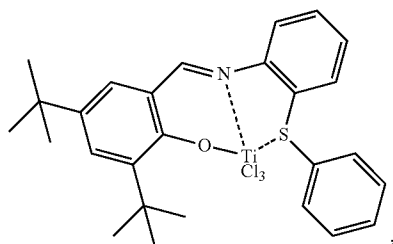
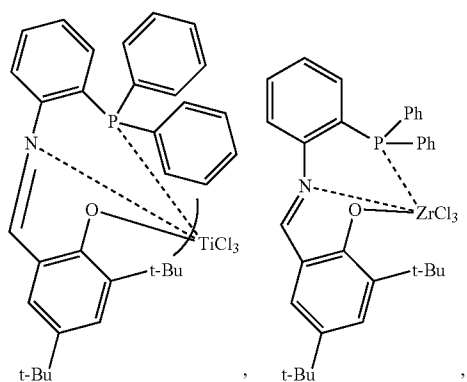
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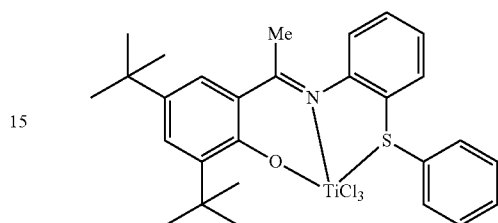
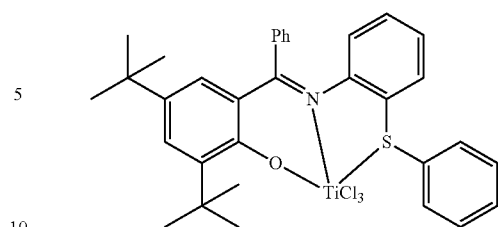


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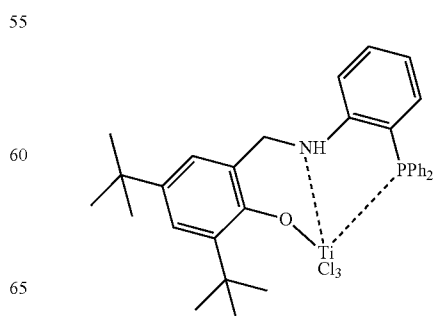
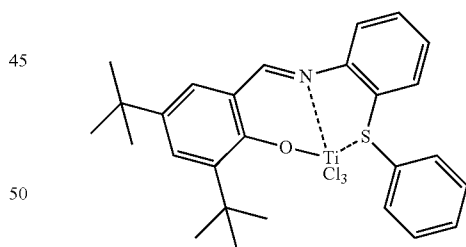
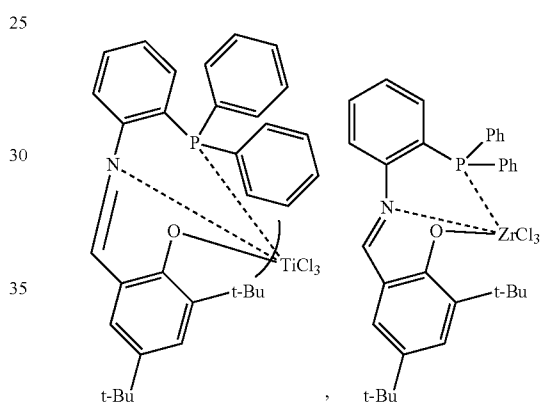
As the nonmetallocene complex, the following compounds can be further exemplified.

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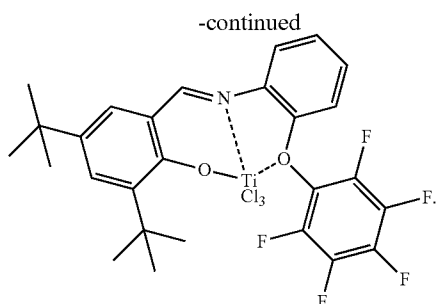
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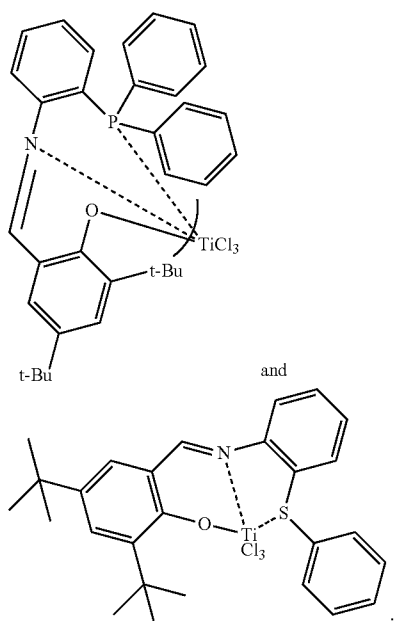
As the nonmetallocene complex, the following compounds can be further exemplified.



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As the nonmetallocene complex, the following compounds can be further exemplified.



The nonmetallocene complexes could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

According to this invention, the multi-dentate ligand in the nonmetallocene complex does not correspond to or comprise the di-ether compound conventionally used in this field as an electron donor compound.

According to this invention, the multi-dentate ligand or the nonmetallocene complex can be produced in line with any process known in this field by a person skilled in the art. For the details of the process, one can refer to for example WO03/010207 or the Chinese Patent Nos. ZL01126323.7 and ZL02110844.7. All the references cited herein are incorporated by reference in their entireties.

According to the first to fourth embodiments of this invention, the porous carrier is mixed with the magnesium compound solution whereby obtaining the slurry.

According to this invention, mixing of the porous carrier with the magnesium compound solution could be conducted by using any conventional process, without any specific limitation. For example, the mixing could be conducted by for example at a temperature ranging from the normal temperature to the temperature at which the magnesium compound solution is prepared, metering the porous carrier into the magnesium compound solution, or metering the magnesium

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compound solution into the porous carrier, and then mixing with each other for 0.1 to 8 hours, such as 0.5 to 4 hours, such as 1 to 2 hours, if necessary, under stirring.

According to this invention, as the amount of the porous carrier to be used, it is desirable that the ratio by weight of the magnesium compound (based on the magnesium compound solid contained in the magnesium compound solution) to the porous carrier is 1:0.1-20, preferably 1:0.5-10, more preferably 1:1-5.

The resultant slurry is a slurry system. Though it is not always necessary, it is preferably for the slurry to stand in a sealed state for a determined duration after preparation, so as to secure uniformity of the system, wherein the duration could be 2 to 48 hours, such as 4 to 24 hours, such as 6 to 18 hours.

The porous carrier is further described as follows.

According to this invention, as the porous carrier, the organic or inorganic porous solid conventionally used in this field as the carrier for producing a supported catalyst can be exemplified.

Specifically, as the organic porous solid, olefin homopolymers or copolymers, vinyl alcohol homopolymers or copolymers, cyclodextrins, polyesters or co-polyesters, polyamides or co-polyamides, vinyl chloride homopolymers or copolymers, acrylic ester homopolymers or copolymers, methacrylic ester homopolymers or copolymers, styrene homopolymers or copolymers, and partly crosslinked products of these homopolymers or copolymers can be exemplified, preferably partly crosslinked styrene polymers (for example one having a crosslinking degree of from 2% to less than 100%).

According to a further embodiment of this invention, the organic porous solid has one or more active functional group(s) for example selected from the group consisting of a hydroxyl group, a primary amino group, a secondary amino group, a sulfonic acid group, a carboxyl group, an amido group, a N-mono substituted amido group, a sulfonamido group, a N-mono substituted sulfonamido group, a mercapto group, an imido group and a hydrazide group, on its surface, wherein the carboxyl group or the hydroxyl group is preferred.

According to a further embodiment of this invention, the organic porous solid is subjected to a thermal activation before use. The thermal activation can be conducted in a normal way. For example, the organic porous solid is treated by heat under a reduced pressure or under an inert gas atmosphere. By an inert gas atmosphere herein, it means that there exists no component capable of reacting with the organic porous solid in the gas atmosphere, or if does exist, only at a rather minor amount. As the inert gas atmosphere, a nitrogen gas or rare gas atmosphere can be exemplified, preferably a nitrogen gas atmosphere. In view of the poor heat resistance, the thermal activation in connection with the organic porous solid should be conducted with the proviso that the inherent structure and composition of the organic porous solid will not be destroyed. Generally, the temperature at which the thermal activation is conducted is from 50 to 400° C., preferably 100-250° C., while the duration for the thermal activation is from 1 to 24 hours, preferably 2 to 12 hours. After thermal activation, the organic porous solid should be stored under a positive pressure under an inert gas atmosphere before use.

As the inorganic porous solid, a refractory oxide of a Group IIA, IIIA, IVA or IVB metal in the Periodic Table of Elements (for example silica (also known as silicon dioxide or silica gel), alumina, magnesia, titania, zirconia, or thorium oxide), or a refractory composite oxide of any of these metals (for example, silica-alumina, magnesia-alumina, titania-silica,

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titania-magnesia, or titania-alumina), and clay, molecular sieve (for example ZSM-5 or MCM-41), mica, montmorillonite, bentonite or kieselguhr can be exemplified. As the inorganic porous solid, the oxide produced by high temperature hydrolysis of a gaseous metal halide or a gaseous silicon compound, for example silica produced by high temperature hydrolysis of silicon tetrachloride, or alumina produced by high temperature hydrolysis of AlCl_3 can be further exemplified.

As the inorganic porous solid, preference is given to silica, alumina, magnesia, silica-alumina, magnesia-alumina, titanic-silica, titanium oxide, molecular sieve and montmorillonite, more preferably silica.

According to this invention, suitable silica can be produced by any conventional process, or is any commercially available one. For example, Grace 955, Grace 948, Grace SP9-351, Grace SP9-485, Grace SP9-10046, Daysion Syloid 245 and Aerosil 812 from the Grace company, ES70, ES70X, ES70Y, ES70W, ES757, EP10X and EP11 from the Ineos company, or CS-2133 and MS-3040 from the PQ company can be exemplified.

According to a further embodiment of this invention, the inorganic porous solid has an active functional group on its surface, for example a hydroxyl group.

According to a further embodiment of this invention, the inorganic porous solid is subjected to a thermal activation before use. The thermal activation can be conducted in a normal way. For example, the inorganic porous solid is treated by heat under a reduced pressure or under an inert gas atmosphere. By an inert gas atmosphere herein, it means that there exists no component capable of reacting with the inorganic porous solid in the gas atmosphere, or if does exist, only at a rather minor amount. As the inert gas atmosphere, a nitrogen gas or rare gas atmosphere can be exemplified, preferably a nitrogen gas atmosphere. Generally, the temperature at which the thermal activation is conducted is from 200 to 800° C., preferably 400-700° C., preferably 400-650° C., while the duration for the thermal activation is from 0.5 to 24 hours, preferably 2 to 12 hours, preferably 4 to 8 hours. After thermal activation, the inorganic porous solid should be stored under a positive pressure under an inert gas atmosphere before use.

According to this invention, the surface area (measured by the BET method) of the porous carrier is generally, but not limiting to, 10 to 1000 m^2/g , or 100 to 600 m^2/g . The pore volume (measured by the nitrogen adsorption method) of the porous carrier is generally 0.1 to 4 cm^3/g , or 0.2 to 2 cm^3/g . The average particle size (measured by a laser particle size analyzer) of the porous carrier is generally 1 to 500 μm , or 1 to 100 μm .

According to this invention, the porous carrier can present in any form, for example, fine powder, particulate, sphere, aggregate, or other form.

According to the first embodiment of this invention, by directly drying the slurry, or by filtering, washing and drying the slurry, preferably directly drying, a freely flowable solid product can be obtained, which corresponds to the supported nonmetallocene catalyst of this invention.

According to the first embodiment of this invention, in the case of directly drying the slurry, any conventional process, for example, drying under an inert gas atmosphere, vacuum drying or vacuum drying under heat, can be used, preferably vacuum drying under heat. The drying is generally conducted at a temperature 5 to 15° C. lower than the boiling point of any solvent in the slurry, which would be a temperature of 30 to 160° C. or 60 to 130° C., while the duration for the drying is generally, not limiting to, 2 to 24 hours.

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According to the first embodiment of this invention, in case of filtering, washing and drying of the slurry, there is no limitation to the process for filtering, washing or drying, and any conventional process conventionally used in this field can be used as needed. According to this invention, the washing can be generally conducted for 1 to 6 times, preferable 2 to 3 times. Herein, the solvent for washing can be the same as or different from that contained in the slurry. The drying can be conducted in a conventional way, preferably as described in connection with the case of directly drying the slurry.

Further, according to the second embodiment of this invention, by metering into the slurry a precipitating agent, solid matter (solid product) is precipitated out of the slurry, whereby obtaining the supported nonmetallocene catalyst of this invention.

Or, according to the fourth embodiment of this invention, by metering into the slurry a precipitating agent, solid matter (solid product) is precipitated out of the slurry, whereby obtaining the composite carrier.

The precipitating agent is further described as follows.

According to this invention, the term "precipitating agent" is explained in a normal sense as known in this field, and refers to a chemically inert liquid capable of lowering the solubility of a solute (for example the magnesium compound) in its solution to the degree that said solute precipitates from the solution as solid matter.

According to this invention, as the precipitating agent, a solvent that represents as a poor solvent for the magnesium compound while as a good solvent for the solvent for dissolving the magnesium compound can be exemplified. For example, an alkane, a cyclic alkane, a halogenated alkane and a halogenated cyclic alkane can be further exemplified.

As the alkane, exemplified is pentane, hexane, heptane, octane, nonane and decane, and the like, such as hexane, heptane and decane, such as hexane.

As the cyclic alkane, exemplified is cyclohexane, cyclopentane, cyclo heptane, cyclo decane, cyclo nonane, and the like, such as cyclo hexane.

As the halogenated alkane, exemplified is dichloro methane, dichloro hexane, dichloro heptane, trichloro methane, trichloro ethane, trichloro butane, dibromo methane, dibromo ethane, dibromo heptane, tribromo methane, tribromo ethane, tribromo butane, and the like.

As the halogenated cyclic alkane, exemplified is chlorinated cyclo pentane, chlorinated cyclo hexane, chlorinated cyclo heptane, chlorinated cyclo octane, chlorinated cyclo nonane, chlorinated cyclo decane, brominated cyclo pentane, brominated cyclo hexane, brominated cyclo heptane, brominated cyclo octane, brominated cyclo nonane, brominated cyclo decane, and the like.

The precipitating agent can be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

The precipitating agent could be added all at once or dropwise, such as all at once. During the precipitation, any stirring means could be used to facilitate uniform dispersion of the precipitating agent throughout the slurry, and eventually facilitate precipitation of the solid product. The stirring means could be in any form, for example, as a stirring paddle, whose rotational speed could be 10 to 1000 r/min.

There is no limitation as to the amount of the precipitating agent to be used, generally, the ratio by volume of the precipitating agent to the solvent for dissolving the magnesium compound is 1:0.2~5, preferably 1:0.5~2, more preferably 1:0.8~1.5.

There is no limitation as to the temperature at which the precipitating agent is, such as the normal temperature. Further, the precipitation process can be generally conducted at the normal temperature as well.

After completely precipitated, the thus obtained solid product is filtered, washed and dried. There is no limitation to the process for filtering, washing or drying, and any conventional process conventionally used in this field can be used as needed.

If needed, the washing can be generally conducted for 1 to 6 times, preferable 2 to 3 times. Herein, the solvent for washing can be the same as or different from the precipitating agent.

The drying can be conducted in line with a conventional process, for example, drying under an inert gas atmosphere, vacuum drying or vacuum drying under heat, preferably drying under an inert gas atmosphere or vacuum drying under heat, most preferably vacuum drying under heat.

The drying is generally conducted at a temperature ranging from the normal temperature to 100° C. for a duration by which the mass in drying will not loss weight any further. For example, in the case wherein tetrahydrofuran is used as the solvent for dissolving the magnesium compound, the drying is generally conducted at about 80° C. under vacuum for a duration of 2 to 12 hours, while toluene is used as the solvent for dissolving the magnesium compound, the drying is generally conducted at about 100° C. under vacuum for a duration of 4 to 24 hours.

Further, according to the third embodiment of this invention, by directly drying the slurry, or by filtering, washing and drying the slurry, preferably directly drying, a freely flowable solid product can be obtained, which corresponds to the composite carrier of this invention.

According to the third embodiment of this invention, in the case of directly drying the slurry, any conventional process, for example, drying under an inert gas atmosphere, vacuum drying or vacuum drying under heat, can be used, preferably vacuum drying under heat. The drying is generally conducted at a temperature 5 to 15° C. lower than the boiling point of any solvent in the slurry, while the duration for the drying is generally, not limiting to, 2 to 24 hours.

According to the third embodiment of this invention, in case of filtering, washing and drying of the slurry, there is no limitation to the process for filtering, washing or drying, and any conventional process conventionally used in this field can be used as needed. If needed, the washing can be generally conducted for 1 to 6 times, preferable 2 to 3 times. Herein, the solvent for washing can be the same as or different from that contained in the slurry. The drying can be conducted in a conventional way, preferably as described in connection with the case of directly drying the slurry.

Then, according to the third and fourth embodiments of this invention, the composite carrier is treated with a chemical treating agent selected from the group consisting of Group IVB metal compounds (referred to as the chemical treating step hereinafter) so as to obtain the supported nonmetallocene catalyst of this invention.

The chemical treating agent is further described as follows.

According to this invention, a Group IVB metal compound is used as the chemical treating agent.

As the Group IVB metal compound, exemplified is a Group IVB metal halide, a Group IVB metal alkylate, a Group IVB metal alkoxylate, a Group IVB metal alkyl halide, and a Group IVB metal alkoxy halide.

As the Group IVB metal halide, the Group IVB metal alkylate, the Group IVB metal alkoxylate, the Group IVB metal alkyl halide and the Group IVB metal alkoxy halide, exemplified is a compound having the following general formula (IV).



wherein,

m is 0, 1, 2, 3, or 4,

n is 0, 1, 2, 3, or 4,

M is a Group IVB metal in the Periodic Table of Elements,

for example, titanium, zirconium, hafnium and the like,

X is a halogen atom, for example, F, Cl, Br, and I, and

R¹ and R² each independently is selected from the group consisting of a C₁-C₁₀ alkyl, for example, methyl, ethyl, propyl, n-butyl, isobutyl and the like, R¹ and R² could be identical to or different from each other.

Specifically, the Group IVB metal halide could be exemplified as for example, titanium tetrafluoride (TiF₄), titanium tetrachloride (TiCl₄), titanium tetrabromide (TiBr₄), titanium tetraiodide (TiI₄), zirconium tetrafluoride (ZrF₄), zirconium tetrachloride (ZrCl₄), zirconium tetrabromide (ZrBr₄), zirconium tetraiodide (ZrI₄), hafnium tetrafluoride (HfF₄), hafnium tetrachloride (HfCl₄), hafnium tetrabromide (HfBr₄), hafnium tetraiodide (HfI₄).

As the Group IVB metal alkylate, exemplified is tetramethyl titanium (Ti(CH₃)₄), tetraethyl titanium (Ti(CH₃CH₂)₄), tetraisobutyl titanium (Ti(i-C₄H₉)₄), tetran-butyl titanium (Ti(C₄H₉)₄), triethyl methyl titanium (Ti(CH₃)(CH₃CH₂)₃), diethyl dimethyl titanium (Ti(CH₃)₂(CH₃CH₂)₂), trimethyl ethyl titanium (Ti(CH₃)₃(CH₃CH₂)), triisobutyl methyl titanium (Ti(CH₃)(i-C₄H₉)₃), diisobutyl dimethyl titanium (Ti(CH₃)₂(i-C₄H₉)₂), trimethyl isobutyl titanium (Ti(CH₃)₃(i-C₄H₉)), triisobutyl ethyl titanium (Ti(CH₃CH₂)(i-C₄H₉)₃), diisobutyl diethyl titanium (Ti(CH₃CH₂)₂(i-C₄H₉)₂), triethyl isobutyl titanium (Ti(CH₃CH₂)₃(i-C₄H₉)), trin-butyl methyl titanium (Ti(CH₃)(C₄H₉)₃), din-butyl dimethyl titanium (Ti(CH₃)₂(C₄H₉)₂), trimethyl n-butyl titanium (Ti(CH₃)₃(C₄H₉)), trin-butyl methyl titanium (Ti(CH₃CH₂)(C₄H₉)₃), din-butyl diethyl titanium (Ti(CH₃CH₂)₂(C₄H₉)₂), triethyl n-butyl titanium (Ti(CH₃CH₂)₃(C₄H₉)), and so on,

tetramethyl zirconium (Zr(CH₃)₄), tetraethyl zirconium (Zr(CH₃CH₂)₄), tetraisobutyl zirconium (Zr(i-C₄H₉)₄), tetran-butyl zirconium (Zr(C₄H₉)₄), triethyl methyl zirconium (Zr(CH₃)(CH₃CH₂)₃), diethyl dimethyl zirconium (Zr(CH₃)₂(CH₃CH₂)₂), trimethyl ethyl zirconium (Zr(CH₃)₃(CH₃CH₂)), triisobutyl methyl zirconium (Zr(CH₃)(i-C₄H₉)₃), diisobutyl dimethyl zirconium (Zr(CH₃)₂(i-C₄H₉)₂), trimethyl isobutyl zirconium (Zr(CH₃)₃(i-C₄H₉)), triisobutyl ethyl zirconium (Zr(CH₃CH₂)(i-C₄H₉)₃), diisobutyl diethyl zirconium (Zr(CH₃CH₂)₂(i-C₄H₉)₂), triethyl isobutyl zirconium (Zr(CH₃CH₂)₃(i-C₄H₉)), trin-butyl methyl zirconium (Zr(CH₃)(C₄H₉)₃), din-butyl dimethyl zirconium (Zr(CH₃)₂(C₄H₉)₂), trimethyl n-butyl zirconium (Zr(CH₃)₃(C₄H₉)), trin-butyl methyl zirconium (Zr(CH₃CH₂)(C₄H₉)₃), din-butyl diethyl zirconium (Zr(CH₃CH₂)₂(C₄H₉)₂), triethyl n-butyl zirconium (Zr(CH₃CH₂)₃(C₄H₉)), and so on,

tetramethyl hafnium (Hf(CH₃)₄), tetraethyl hafnium (Hf(CH₃CH₂)₄), tetraisobutyl hafnium (Hf(i-C₄H₉)₄), tetran-butyl hafnium (Hf(C₄H₉)₄), triethyl methyl hafnium (Hf(CH₃)(CH₃CH₂)₃), diethyl dimethyl hafnium (Hf(CH₃)₂(CH₃CH₂)₂), trimethyl ethyl hafnium (Hf(CH₃)₃(CH₃CH₂)), triisobutyl methyl hafnium (Hf(CH₃)(i-C₄H₉)₃), diisobutyl dimethyl hafnium (Hf(CH₃)₂(i-C₄H₉)₂), trimethyl isobutyl hafnium (Hf(CH₃)₃(i-C₄H₉)), triisobutyl ethyl hafnium (Hf(CH₃CH₂)(i-C₄H₉)₃), diisobutyl diethyl hafnium (Hf(CH₃CH₂)₂(i-C₄H₉)₂), triethyl isobutyl hafnium (Hf(CH₃CH₂)₃(i-C₄H₉)), trin-butyl methyl hafnium (Hf(CH₃)(C₄H₉)₃), din-butyl dimethyl hafnium (Hf(CH₃)₂(C₄H₉)₂), trimethyl n-butyl hafnium (Hf(CH₃)₃(C₄H₉)), trin-butyl methyl hafnium (Hf(CH₃CH₂)(C₄H₉)₃), din-butyl diethyl hafnium (Hf(CH₃CH₂)₂(C₄H₉)₂), triethyl n-butyl hafnium (Hf(CH₃CH₂)₃(C₄H₉)), and so on.

trimethoxy bromo titanium ($\text{TiBr}(\text{OCH}_3)_3$), triethoxy bromo titanium ($\text{TiBr}(\text{OCH}_3\text{CH}_2)_3$), triisobutoxy bromo titanium ($\text{TiBr}(\text{i-OC}_4\text{H}_9)_3$), tri-n-butoxy bromo titanium ($\text{TiBr}(\text{OC}_4\text{H}_9)_3$), dimethoxy dibromo titanium ($\text{TiBr}_2(\text{OCH}_3)_2$), diethoxy dibromo titanium ($\text{TiBr}_2(\text{OCH}_3\text{CH}_2)_2$), diisobutoxy dibromo titanium ($\text{TiBr}_2(\text{i-OC}_4\text{H}_9)_2$), tri-n-butoxy bromo titanium ($\text{TiBr}(\text{OC}_4\text{H}_9)_3$), methoxy tribromo titanium ($\text{Ti}(\text{OCH}_3\text{Br}_3)$), ethoxy tribromo titanium ($\text{Ti}(\text{OCH}_3\text{CH}_2\text{Br}_3)$), isobutoxy tribromo titanium ($\text{Ti}(\text{i-C}_4\text{H}_9\text{Br}_3)$), n-butoxy tribromo titanium ($\text{Ti}(\text{OC}_4\text{H}_9\text{Br}_3)$).

trimethoxy chloro zirconium ($\text{ZrCl}(\text{OCH}_3)_3$), triethoxy chloro zirconium ($\text{ZrCl}(\text{OCH}_3\text{CH}_2)_3$), triisobutoxy chloro zirconium ($\text{ZrCl}(\text{i-OC}_4\text{H}_9)_3$), tri-n-butoxy chloro zirconium ($\text{ZrCl}(\text{OC}_4\text{H}_9)_3$), dimethoxy dichloro zirconium ($\text{ZrCl}_2(\text{OCH}_3)_2$), diethoxy dichloro zirconium ($\text{ZrCl}_2(\text{OCH}_3\text{CH}_2)_2$), diisobutoxy dichloro zirconium ($\text{ZrCl}_2(\text{i-OC}_4\text{H}_9)_2$), tri-n-butoxy chloro zirconium ($\text{ZrCl}(\text{OC}_4\text{H}_9)_3$), methoxy trichloro zirconium ($\text{Zr}(\text{OCH}_3)\text{Cl}_3$), ethoxy trichloro zirconium ($\text{Zr}(\text{OCH}_3\text{CH}_2)\text{Cl}_3$), isobutoxy trichloro zirconium ($\text{Zr}(\text{i-C}_4\text{H}_9)\text{Cl}_3$), n-butoxy trichloro zirconium ($\text{Zr}(\text{OC}_4\text{H}_9)\text{Cl}_3$), trimethoxy bromo zirconium ($\text{ZrBr}(\text{OCH}_3)_3$), triethoxy bromo zirconium ($\text{ZrBr}(\text{OCH}_3\text{CH}_2)_3$), triisobutoxy bromo zirconium ($\text{ZrBr}(\text{i-OC}_4\text{H}_9)_3$), tri-n-butoxy bromo zirconium ($\text{ZrBr}(\text{OC}_4\text{H}_9)_3$), dimethoxy dibromo zirconium ($\text{ZrBr}_2(\text{OCH}_3)_2$), diethoxy dibromo zirconium ($\text{ZrBr}_2(\text{OCH}_3\text{CH}_2)_2$), diisobutoxy dibromo zirconium ($\text{ZrBr}_2(\text{i-OC}_4\text{H}_9)_2$), tri-n-butoxy bromo zirconium ($\text{ZrBr}(\text{OC}_4\text{H}_9)_3$), methoxy tribromo zirconium ($\text{Zr}(\text{OCH}_3)\text{Br}_3$), ethoxy tribromo zirconium ($\text{Zr}(\text{OCH}_3\text{CH}_2)\text{Br}_3$), isobutoxy tribromo zirconium ($\text{Zr}(\text{i-C}_4\text{H}_9)\text{Br}_3$), n-butoxy tribromo zirconium ($\text{Zr}(\text{OC}_4\text{H}_9)\text{Br}_3$), trimethoxy chloro hafnium ($\text{HfCl}(\text{OCH}_3)_3$), triethoxy chloro hafnium ($\text{HfCl}(\text{OCH}_3\text{CH}_2)_3$), triisobutoxy chloro hafnium ($\text{HfCl}(\text{i-OC}_4\text{H}_9)_3$), tri-n-butoxy chloro hafnium ($\text{HfCl}(\text{OC}_4\text{H}_9)_3$), dimethoxy dichloro hafnium ($\text{HfCl}_2(\text{OCH}_3)_2$), diethoxy dichloro hafnium ($\text{HfCl}_2(\text{OCH}_3\text{CH}_2)_2$), diisobutoxy dichloro hafnium ($\text{HfCl}_2(\text{i-OC}_4\text{H}_9)_2$), tri-n-butoxy chloro hafnium ($\text{HfCl}(\text{OC}_4\text{H}_9)_3$), methoxy trichloro hafnium ($\text{Hf}(\text{OCH}_3)\text{Cl}_3$), ethoxy trichloro hafnium ($\text{Hf}(\text{OCH}_3\text{CH}_2)\text{Cl}_3$), isobutoxy trichloro hafnium ($\text{Hf}(\text{i-C}_4\text{H}_9)\text{Cl}_3$), n-butoxy trichloro hafnium ($\text{Hf}(\text{OC}_4\text{H}_9)\text{Cl}_3$), trimethoxy bromo hafnium ($\text{HfBr}(\text{OCH}_3)_3$), triethoxy bromo hafnium ($\text{HfBr}(\text{OCH}_3\text{CH}_2)_3$), triisobutoxy bromo hafnium ($\text{HfBr}(\text{i-OC}_4\text{H}_9)_3$), tri-n-butoxy bromo hafnium ($\text{HfBr}(\text{OC}_4\text{H}_9)_3$), dimethoxy dibromo hafnium ($\text{HfBr}_2(\text{OCH}_3)_2$), diethoxy dibromo hafnium ($\text{HfBr}_2(\text{OCH}_3\text{CH}_2)_2$), diisobutoxy dibromo hafnium ($\text{HfBr}_2(\text{i-OC}_4\text{H}_9)_2$), tri-n-butoxy bromo hafnium ($\text{HfBr}(\text{OC}_4\text{H}_9)_3$), methoxy tribromo hafnium ($\text{Hf}(\text{OCH}_3)\text{Br}_3$), ethoxy tribromo hafnium ($\text{Hf}(\text{OCH}_3\text{CH}_2)\text{Br}_3$), isobutoxy tribromo hafnium ($\text{Hf}(\text{i-C}_4\text{H}_9)\text{Br}_3$), n-butoxy tribromo hafnium ($\text{Hf}(\text{OC}_4\text{H}_9)\text{Br}_3$).

As the Group IVB metal compound, preference is given to the Group IVB metal halide, such as TiCl_4 , TiBr_4 , ZrCl_4 , ZrBr_4 , HfCl_4 and HfBr_4 , such as TiCl_4 and ZrCl_4 .

The Group IVB metal compound could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

When the chemical treating agent presents as a liquid at the normal temperature, the chemical treating agent can be used by directly dropwise adding a predetermined amount of the chemical treating agent to a reaction subject to be treated with said chemical treating agent (i.e. the aforesaid composite carrier).

When the chemical treating agent presents a solid at the normal temperature, for ease of metering and handling, it is preferably to use said chemical treating agent in the form of a solution. Of course, when the chemical treating agent presents a liquid at the normal temperature, said chemical treating agent can be also used in the form of a solution if needed, without any specific limitation.

In preparation of the solution of the chemical treating agent, there is no limitation as to the solvent to be used herein, as long as the solvent is capable of dissolving the chemical treating agent.

Specifically, as the solvent, exemplified is a C_{5-12} alkane or a halogenated C_{5-12} alkane, for example pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, cyclohexane, chloro pentane, chloro hexane, chloro heptane,

chloro octane, chloro nonane, chloro decane, chloro undecane, chloro dodecane, chloro cyclohexane and so on, preferably pentane, hexane, decane and cyclohexane, most preferably hexane.

The solvent could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

It is obvious that a solvent capable of extracting the magnesium compound is not used herein to dissolve the chemical treating agent, for example an ether based solvent, for example tetrahydrofuran.

Further, there is no limitation as to the concentration of the chemical treating agent in the solution, which could be determined as needed, as long as it is sufficient for the solution to deliver the predetermined amount of the chemical treating agent for the chemical treatment. As aforesaid, if the chemical treating agent presents as a liquid, it is convenient to use said chemical treating agent as such for the treatment, while it is also acceptable to convert it into a solution before use. Generally, the molar concentration of the chemical treating agent in its solution is, but not limiting to, 0.01 to 1.0 mol/L.

As a process for conducting the chemical treatment, exemplified is a process wherein, when a solid chemical treating agent (for example ZrCl_4) is used, first of all, a solution of the chemical treating agent is prepared, then the chemical treating agent is added (preferably dropwise) at a predetermined amount to the composite carrier to be treated, or when a liquid chemical treating agent (for example TiCl_4) is used, it is acceptable to add (preferably dropwise) a predetermined amount of the chemical treating agent as such (or after prepared into a solution) to the composite carrier. Then, the chemical treating reaction continues (facilitated by any stirring means, if necessary) at a reaction temperature ranging from -30°C . to 60°C . (preferably -20°C . to 30°C .) for 0.5 to 24 hours, preferably 1 to 8 hours, more preferably 2 to 6 hours. Then, the resultant is filtrated, washed and dried.

According to this invention, the filtrating, washing (generally for 1 to 8 times, preferably 2 to 6 times, most preferably 2 to 4 times) and drying can be conducted in a conventional manner, wherein the solvent for washing could be the same as that used for dissolving the chemical treating agent.

According to this invention, as the amount of the chemical treating agent to be used, it is preferably that the ratio by molar of the magnesium compound (based on Mg, solid basis) to the chemical treating agent (based on the Group IVB metal, for example Ti) is 1:0.01-1, preferably 1:0.01-0.50, more preferably 1:0.10-0.30.

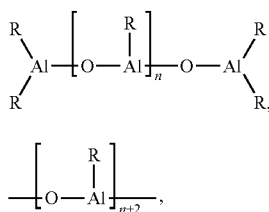
According to a further embodiment of this invention, the present process for producing a supported nonmetallocene catalyst further comprises a step of pre-treating the composite carrier with an assistant chemical treating agent selected from the group consisting of an aluminoxane, an alkylaluminum and any combination thereof before treating the composite carrier with the chemical treating agent, referred to as the pre-treating step hereinafter. Then, the chemical treating step is conducted by using the chemical treating agent in the same way as aforesaid, with the only difference of replacing the composite carrier with the thus pre-treated composite carrier.

The assistant chemical treating agent is further described as follows.

According to this invention, as the assistant chemical treating agent, exemplified is aluminoxane and alkylaluminum.

As the aluminoxane, exemplified is a linear aluminoxane $((\text{R})(\text{R})\text{Al}-(\text{Al}(\text{R})-\text{O})_n-\text{O}-\text{Al}(\text{R})(\text{R}))$ having the following formula (I), and a cyclic aluminoxane $(-\text{Al}(\text{R})-\text{O}-)_{n+2}$ having the following formula (II).

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wherein the Rs are identical to or different from one another, preferably identical to one another, and each independently is selected from the group consisting of a C₁-C₈ alkyl, preferably methyl, ethyl, and iso-butyl, most preferably methyl, n is an integer of 1 to 50, preferably of 10 to 30.

Specifically, the aluminosilane could be preferably selected from the group consisting of methyl aluminosilane, ethyl aluminosilane, isobutyl aluminosilane and n-butyl aluminosilane, preferably methyl aluminosilane (MAO) and isobutyl aluminosilane (IBAO).

The aluminosilane could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

As the alkylaluminum, exemplified is a compound having a general formula (III) as follows:



wherein the Rs are identical to or different from one another, preferably identical to one another, and is each independently selected from the group consisting of a C₁-C₈ alkyl, preferably methyl, ethyl and iso-butyl, most preferably methyl.

Specifically, the alkylaluminum could be selected from the group consisting of trimethyl aluminum (Al(CH₃)₃), triethyl aluminum (Al(CH₃CH₂)₃), tripropyl aluminum (Al(C₃H₇)₃), triisobutyl aluminum (Al(i-C₄H₉)₃), tri-n-butyl aluminum (Al(C₄H₉)₃), triisooamyl aluminum (Al(i-C₅H₁₁)₃), tri-n-amyl aluminum (Al(C₅H₁₁)₃), trihexyl aluminum (Al(C₆H₁₃)₃), tri-iso-hexyl aluminum (Al(i-C₆H₁₃)₃), diethyl methyl aluminum (Al(CH₃)(CH₃CH₂)₂) and ethyl dimethyl aluminum (Al(CH₃CH₂)(CH₃)₂), and the like, wherein preference is given to trimethyl aluminum, triethyl aluminum, triisobutyl aluminum and tripropyl aluminum, most preferably triethyl aluminum and triisobutyl aluminum.

The alkylaluminum could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

According to this invention, as the assistant chemical treating agent, used could be only the alkylaluminum or only the aluminosilane, or any mixture of the alkylaluminum and the aluminosilane. There is no limitation as to the ratio between any two or more components in the mixture, which could be determined as needed.

According to this invention, the assistant chemical treating agent is generally used in the form of a solution. In preparation of the solution of the assistant chemical treating agent, there is no limitation as to the solvent to be used herein, as long as the solvent can dissolve the assistant chemical treating agent.

Specifically, as the solvent, exemplified is a C₅₋₁₂ alkane or a halogenated C₅₋₁₂ alkane, for example pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, cyclohexane, chloro pentane; chloro hexane, chloro heptane, chloro octane, chloro nonane, chloro decane, chloro undecane, chloro dodecane, chloro cyclohexane and so on, preferably pentane, hexane, decane and cyclohexane, most preferably hexane.

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It is obvious that a solvent capable of extracting the magnesium compound is not used herein to dissolve the assistant chemical treating agent, for example an ether based solvent, for example tetrahydrofuran.

The solvent could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

Further, there is no limitation as to the concentration of the assistant chemical treating agent in the solution, which could be determined as needed, as long as it is sufficient for the solution to deliver a predetermined amount of the assistant chemical treating agent for the pre-treatment.

As a process for conducting the pre-treatment, exemplified is a process wherein, first of all, a solution of the assistant chemical treating agent is prepared, then at a temperature ranging from -30° C. to 60° C. (preferably -20° C. to 30° C.), the assistant chemical treating agent solution (containing a predetermined amount of the assistant chemical treating agent) is metering (preferably dropwise) into the composite carrier to be pre-treated with said assistant chemical treating agent, or the composite carrier is metering into the assistant chemical treating agent solution, so as to form a reaction mixture. Then, the reaction continues (facilitated by any stirring means, if necessary) for 1 to 8 hours, preferably 2 to 6 hours, more preferably 3 to 4 hours. Then, the thus obtained product is separated from the reaction mixture by filtrating, washing (for 1 to 6 times, preferably 1 to 3 times) and optional drying. Or alternatively, the thus obtained product is directly used in the next step (i.e. the aforesaid chemical treating step) in the form of the reaction mixture without being subject to the separation beforehand. In this case, the reaction mixture contains a certain amount of solvent, and for this reason, the amount of the solvent involved in said next step could be reduced accordingly.

According to this invention, as the amount of the assistant chemical treating agent to be used, it is preferably that the ratio by molar of the magnesium compound (based on Mg, on a solid basis) to the assistant chemical treating agent (based on Al) is 1:0-1.0, preferably 1:0-0.5, more preferably 1:0.1-0.5.

It is known that any of the aforementioned processes and steps is preferably carried out under a substantial water-free and oxygen-free condition. By substantial water-free and oxygen-free condition, it means that water and oxygen in the system concerned is continuously controlled to be less than 10 ppm. Further, the support nonmetallocene catalyst according to this invention, after prepared, is usually stored under a sealed condition under a slightly positive pressure before use.

According to this invention, as the amount of the nonmetallocene complex to be used, it is preferably that the ratio by molar of the magnesium compound (based on Mg, on a solid basis) to the nonmetallocene complex is 1:0.01-1, preferably 1:0.04-0.4, more preferably 1:0.08-0.2.

According to this invention, as the amount of the solvent for dissolving the magnesium compound to be used, it is preferably that the ratio of the magnesium compound (on a solid basis) to the solvent is 1 mol:75-400 ml, preferably 1 mol:150-300 ml, more preferably 1 mol:200-250 ml.

According to this invention, as the amount of the porous carrier to be used, it is preferably that the ratio by weight of the magnesium compound (on a solid basis) to the porous carrier is 1:0.1-20, preferably 1:0.5-10, more preferably 1:1-5.

According to this invention, as the amount of the precipitating agent to be used, it is preferably that the ratio by volume of the precipitating agent to the solvent for dissolving the magnesium compound is 1:0.2-5, preferably 1:0.5-2, more preferably 1:0.8-1.5.

According to this invention, as the amount of the chemical treating agent to be used, it is preferably that the ratio by molar of the magnesium compound (based on Mg, on a solid basis) to the chemical treating agent (based on the Group IVB metal, for example Ti) is 1:0.01-1, preferably 1:0.01-0.50, more preferably 1:0.10-0.30.

According to this invention, as the amount of the assistant chemical treating agent to be used, it is preferably that the ratio by molar of the magnesium compound (based on Mg, on a solid basis) to the assistant chemical treating agent (based on Al) is 1:0-1.0, preferably 1:0-0.5, more preferably 1:0.1-0.5.

In one embodiment, this invention relates to a supported nonmetallocene catalyst produced in line with the process according to any of the first to fourth embodiments of this invention, also referred to as a supported nonmetallocene catalyst for olefin polymerization.

In a further embodiment according to this invention, this invention relates to an olefin homopolymerization/copolymerization process, wherein the supported nonmetallocene catalyst of this invention is used as the catalyst for olefin polymerization, to homopolymerize or copolymerize olefin(s).

In the context of the olefin homopolymerization/copolymerization process of this invention, one can directly refer to the prior art for any content or information that has not been expressively and specifically described hereinafter, for example, the reactor for polymerization, the amount of olefin(s), the way by which the catalyst or olefin is introduced, unneccessitating the need of detailing same further herein.

According to the present olefin homopolymerization/copolymerization process, the supported nonmetallocene catalyst of this invention is used as the main catalyst, one or more selected from the group consisting of an aluminoxane, an alkylaluminum, a halogenated alkyl aluminum, a fluoroborane, an alkylboron and an alkylboron ammonium salt is used as the co-catalyst, to homopolymerize or copolymerize olefin.

As the way of adding the main catalyst and the co-catalyst to the polymerization system, exemplified is a way wherein the main catalyst is added prior to the co-catalyst, or vice versa, or the main catalyst and the co-catalyst contact with each other by mixing and then added altogether, or separately but simultaneously added. As the way of adding the main catalyst and the co-catalyst separately, exemplified is the case wherein the main catalyst and the co-catalyst are successively added to one feed line or multiple feed lines. When the main catalyst and the co-catalyst are to be added separately but simultaneously, multiple feed lines are required. For a continuous polymerization, the way of simultaneously and continuously adding to multiple feed lines is preferred, while for a batch polymerization, the way of mixing the main catalyst and the co-catalyst with each other and then adding to one feed line altogether, or adding to a feed line the co-catalyst and then adding the main catalyst to the same feed line, is preferred.

There is no limitation as to how to conduct the olefin homopolymerization/copolymerization, any conventional process known to a person skilled in the art can be used, for example, a slurry process, an emulsion process, a solution process, a bulk process or a gas phase process, preferably the slurry process or the gas phase process.

According to this invention, as the olefin to be used, exemplified is a C₂ to C₁₀ mono-olefin, a diolefin, a cyclic olefin and other ethylenic unsaturated compounds.

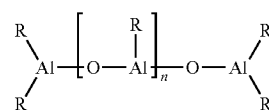
Specifically, as the C₂ to C₁₀ mono-olefin, exemplified is ethylene, propylene, 1-butene, 1-hexene, 1-heptene, 4-me-

thyl-1-pentene, 1-octene, 1-decene, 1-undecene, 1-dodecene and styrene. As the cyclic olefin, exemplified is 1-cyclopentene and norbornene. As the diolefin, exemplified is 1,4-butadiene, 2,5-pentadiene, 1,6-hexadiene, norbornadiene and 1,7-octadiene. As the other ethylenic unsaturated compound, exemplified is vinyl acetate, and (meth)acrylate. This invention prefers the homopolymerization of ethylene, or the copolymerization of ethylene with propylene, 1-butene or 1-hexene.

According to this invention, by homopolymerization, it refers to the polymerization of a single kind of olefin, by copolymerization, it refers to the polymerization between two or more of the aforesaid olefins.

According to this invention, the co-catalyst is selected from the group consisting of an aluminoxane, an alkylaluminum, a halogenated alkyl aluminum, a fluoroborane, an alkylboron and an alkylboron ammonium salt, such as the aluminoxane and the alkylaluminum.

As the aluminoxane, exemplified is a linear aluminoxane ((R)(R)Al—(Al(R)—O)_n—O—Al(R)(R)) having the following formula (I-1), and a cyclic aluminoxane ((—Al(R)—O—)_{n+2}) having the following formula (II-1).



wherein the Rs are identical to or different from one another, preferably identical to one another, and each independently is selected from the group consisting of a C₁-C₈ alkyl, preferably methyl, ethyl, and iso-butyl, most preferably methyl, n is an integer of 1 to 50, preferably of 10 to 30.

Specifically, the aluminoxane could be preferably selected from the group consisting of methyl aluminoxane, ethyl aluminoxane, isobutyl aluminoxane and n-butyl aluminoxane, preferably methyl aluminoxane (MAO) and isobutyl aluminoxane (IBAO), most preferably methyl aluminoxane (MAO).

The aluminoxane could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

As the alkylaluminum, exemplified is a compound having a general formula (III-1) as follows:



wherein the Rs are identical to or different from one another, preferably identical to one another, and is each independently selected from the group consisting of a C₁-C₈ alkyl, preferably methyl, ethyl and iso-butyl, most preferably methyl.

Specifically, the alkylaluminum could be selected from the group consisting of trimethyl aluminum (Al(CH₃)₃), triethyl aluminum (Al(CH₃CH₂)₃), tripropyl aluminum (Al(C₃H₇)₃), triisobutyl aluminum (Al(i-C₄H₉)₃), tri-n-butyl aluminum (Al(C₄H₉)₃), triisooamyl aluminum (Al(i-C₅H₁₁)₃), tri-n-amyl aluminum (Al(C₅H₁₁)₃), tri-hexyl aluminum (Al(C₆H₁₃)₃), tri-iso-hexyl aluminum (Al(i-C₆H₁₃)₃), diethyl methyl aluminum (Al(CH₃)(CH₃CH₂)₂) and ethyl dimethyl aluminum (Al(CH₃CH₂)(CH₃)₂), and the like, wherein preference is given to trimethyl aluminum, triethyl aluminum,

triisobutyl aluminum and tripropyl aluminum, more preferably triethyl aluminum and triisobutyl aluminum, most preferably triethyl aluminum.

The alkylaluminum could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

As the halogenated alkyl aluminum, the fluoroborane, the alkylboron and the alkylboron ammonium salt, exemplified is one conventionally used in this field, but without any limitation thereto.

Further, according to this invention, the co-catalyst could be used with one kind or as a mixture of two or more kinds of the aforesaid co-catalysts at any ratio therebetween as needed, but without any limitation thereto.

According to this invention, depending on how the olefin homopolymerization/copolymerization is conducted, a solvent for polymerization may be involved.

As the solvent for polymerization, one conventionally used in this field for olefin homopolymerization/copolymerization can be used, but without any limitation thereto.

As the solvent for polymerization, exemplified is a C₄₋₁₀ alkane (for example, butane, pentane, hexane, heptane, octane, nonane, or decane), a halogenated C₁₋₁₀ alkane (for example, dichloro methane), an aromatic hydrocarbon based solvent (for example toluene or xylene), and so on. Hexane is preferred for this purpose.

The solvent for polymerization could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

According to this invention, the polymerization pressure under which the olefin homopolymerization/copolymerization is conducted is generally between 0.1 to 10 MPa, preferably 0.1 to 4 MPa, most preferably 1 to 3 MPa, but without any limitation thereto. According to this invention, the polymerization temperature at which the olefin homopolymerization/copolymerization is conducted is generally from -40° C. to 200° C., preferably 10° C. to 100° C., more preferably 40° C. to 90° C., but without any limitation thereto.

Further, according to this invention, the olefin homopolymerization/copolymerization can be conducted in the presence of or in the absence of hydrogen gas. If presents, the partial pressure of hydrogen gas may generally account for 0.01 to 99% (preferably 0.01 to 50%) of the polymerization pressure, but without any limitation thereto.

According to the olefin homopolymerization/copolymerization process of this invention, the ratio by molar of the co-catalyst (based on Al or B) to the supported nonmetallocene catalyst (based on the central metal atom M) is generally 1 to 1000:1, preferably 10 to 500:1, more preferably 15 to 300:1, but without any limitation thereto.

EXAMPLE

The present invention is further illustrated by using the following examples, not limiting to same.

The bulk density of the polymer was measured according to the Chinese Standard GB 1636-79 (unit: g/cm³).

The content of the Group IVB metal (for example Ti) and the content of the Mg element in the supported nonmetallocene catalyst were determined by the ICP-AES method, while the content of the nonmetallocene ligand was determined by the element analysis method.

The polymerization activity of the catalyst was calculated as follows.

Upon completion of the polymerization, the polymer product in the reactor was filtered and dried, and then weighed for its weight (by mass). Then, the polymerization activity of the catalyst was expressed by a value obtained by dividing the

weight of the polymer product by the weight (by mass) of the supported nonmetallocene catalyst used (unit: kg polymer per 1 g Cat).

The molecular weights Mw, Mn and the molecular weight distribution (Mw/Mn) of the polymer were determined at a temperature of 150° C. by using the GPC V2000 type gel permeation chromatographer (from WATERS Co., USA), with o-trichlorobenzene as the solvent.

The viscosity averaged molecular weight of the polymer was calculated as follows.

The intrinsic viscosity of the polymer was determined according to the standard ASTM D4020-00 by using a high temperature dilution type Ubbelohde viscometer (with a capillary inner diameter of 0.44 mm, a thermostatic bath media of 300# silicon oil, the solvent for dilution of decalin and a temperature of 135° C.), and then the viscosity averaged molecular weight Mv of the polymer was calculated in line with the following formula.

$$Mv = 5.37 \times 10^4 \times [\eta]^{1.37}$$

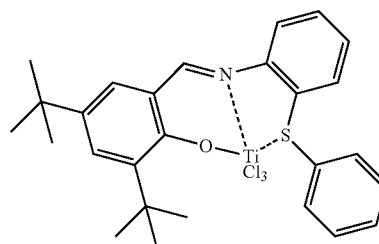
wherein, η is the intrinsic viscosity.

Example I

Corresponding to the First Embodiment

Example I-1

Anhydrous magnesium chloride was used as the magnesium compound, tetrahydrofuran was used as the solvent for dissolving the magnesium compound and the nonmetallocene complex, silica gel (ES757, from the Ineos Company) was used as the porous carrier, the compound represented by



was used as the nonmetallocene complex.

The silica gel was thermally activated by continuously calcinating at 600° C. under a N₂ atmosphere for 4 hours before use.

5 g of the anhydrous magnesium chloride and the nonmetallocene complex were weighed, tetrahydrofuran was added thereto to completely dissolve same at the normal temperature. Then, the thermally activated silica gel was added thereto, after stirring for 2 hours, the resultant was uniformly heated to 90° C. and directly vacuum dried, to obtain the supported nonmetallocene catalyst.

In this example, the ratio of magnesium chloride to tetrahydrofuran was 1 mol:210 ml, the ratio by molar of magnesium chloride to the nonmetallocene complex was 1:0.08, and the ratio by weight of magnesium chloride to the porous carrier was 1:2.

The thus obtained supported nonmetallocene catalyst was named as CAT-I-1.

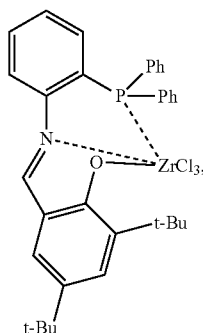
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Example I-2

Substantially the same as the Example I-1, except for the following changes:

The porous carrier was changed to silica gel (955, from the Grace Company), which has been thermally activated by continuously calcinating at 400° C. under a N₂ gas atmosphere for 8 hours.

The nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to toluene, and the magnesium compound solution was vacuum dried at 100° C.

In this example, the ratio of the magnesium compound to toluene was 1 mol:150 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.15, and the ratio by weight of the magnesium compound to the porous carrier was 1:4.

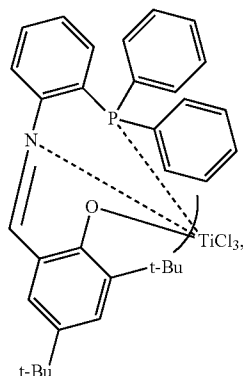
The thus obtained supported nonmetallocene catalyst was named as CAT-I-2.

Example I-3

Substantially the same as the Example I-1, except for the following changes:

The porous carrier was changed to Al₂O₃, which has been thermally activated by continuously calcinating at 700° C. under a N₂ gas atmosphere for 6 hours.

The magnesium compound was changed to anhydrous magnesium bromide (MgBr₂), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to ethyl benzene, and the magnesium compound solution was vacuum dried at 110° C.

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In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:250 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.20, and the ratio by weight of the magnesium compound to the porous carrier was 1:1.

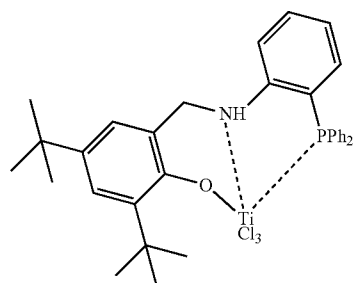
The thus obtained supported nonmetallocene catalyst was named as CAT-I-3.

Example I-4

Substantially the same as the Example I-1, except for the following changes:

The porous carrier was changed to a mixed oxide of silica and MgO (at a ratio by weight of 1:1), which has been thermally activated by continuously calcinating at 600° C. under an Ar gas atmosphere for 4 hours.

The magnesium compound was changed to ethoxy magnesium chloride (MgCl(OC₂H₅)), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to xylene, and the magnesium compound solution was vacuum dried at 150° C.

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:300 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.04, and the ratio by weight of the magnesium compound to the porous carrier was 1:3.

The thus obtained supported nonmetallocene catalyst was named as CAT-I-4.

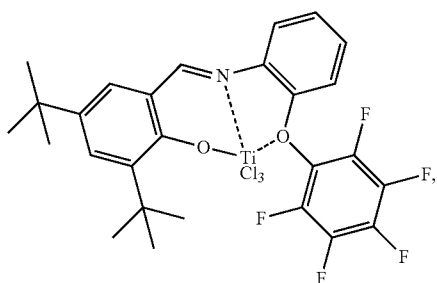
Example I-5

Substantially the same as the Example I-1, except for the following changes:

The porous carrier was changed to montmorillonite, which has been thermally activated by continuously calcinating at 400° C. under a N₂ gas atmosphere for 8 hours.

The magnesium compound was changed to butoxy magnesium bromide (MgBr(OC₄H₉)), the nonmetallocene complex was changed to

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the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to diethyl benzene, and the magnesium compound solution was vacuum dried at 110° C.

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:400 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.30, and the ratio by weight of the magnesium compound to the porous carrier was 1:5.

The thus obtained supported nonmetallocene catalyst was named as CAT-I-5.

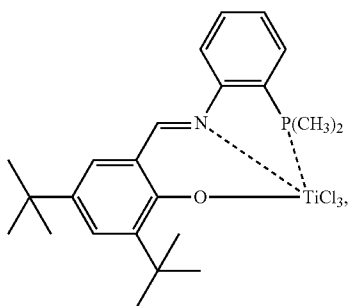
Example I-6

Substantially the same as the Example I-1, except for the following changes:

The porous carrier was changed to polystyrene, which has been thermally activated by continuously drying at 85° C. under a N₂ gas atmosphere for 12 hours.

The magnesium compound was changed to methyl magnesium chloride

(Mg(CH₃)Cl), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to chloro toluene, and the magnesium compound solution was vacuum dried at 120° C.

In this example, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.10, and the ratio by weight of the magnesium compound to the porous carrier was 1:10.

The thus obtained supported nonmetallocene catalyst was named as CAT-I-6.

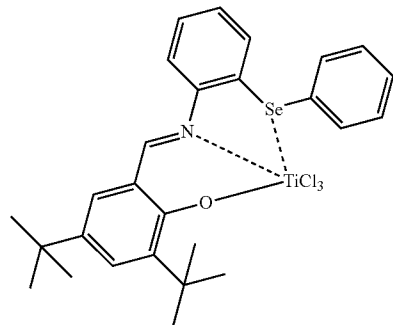
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Example I-7

Substantially the same as the Example I-1, except for the following changes:

The porous carrier was changed to kieselguhr, which has been thermally activated by continuously calcinating at 500° C. under a N₂ gas atmosphere for 8 hours.

The magnesium compound was changed to ethyl magnesium chloride (Mg(C₂H₅)Cl), the nonmetallocene complex was changed to



and the magnesium compound solution was vacuum dried at 60° C.

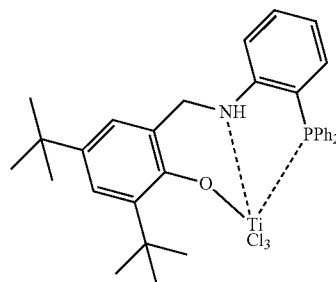
In this example, the ratio by weight of the magnesium compound to the porous carrier was 1:0.5.

The thus obtained supported nonmetallocene catalyst was named as CAT-I-7.

Example I-8

Substantially the same as the Example I-1, except for the following changes:

The magnesium compound was changed to ethyl magnesium (Mg(C₂H₅)₂), the nonmetallocene complex was changed to



The thus obtained supported nonmetallocene catalyst was named as CAT-I-8.

Example I-9

Substantially the same as the Example I-1, except for the following changes:

The magnesium compound was changed to methyl ethoxy magnesium (Mg(OC₂H₅)(CH₃)).

The thus obtained supported nonmetallocene catalyst was named as CAT-I-9.

Example I-10

Substantially the same as the Example I-1, except for the following changes:

The magnesium compound was changed to ethyl n-butoxy magnesium ($\text{Mg}(\text{OC}_4\text{H}_9)(\text{C}_2\text{H}_5)$).

The thus obtained supported nonmetallocene catalyst was named as CAT-I-10.

Reference Example I-1-A

Substantially the same as the Example I-1, except for the following changes:

The ratio by molar of magnesium chloride to the nonmetallocene complex was changed to 1:0.16.

The thus obtained catalyst was named as CAT-I-1-A.

Reference Example I-1-B

Substantially the same as the Example I-1, except for the following changes:

The ratio by molar of magnesium chloride to the nonmetallocene complex was changed to 1:0.04.

The thus obtained catalyst was named as CAT-I-1-B.

Reference Example I-1-C

Substantially the same as the Example I-1, except for the following changes:

In preparation of the catalyst, 60 ml hexane was added to the slurry to precipitate same, which was then filtered, washed with hexane for 3 times (60 ml per time), and finally vacuum dried at 60° C.

The thus obtained catalyst was named as CAT-I-1-C.

Application Example I

The catalysts CAT-I-1 to CAT-I-9, CAT-I-1-A to CAT-I-1-C obtained from the aforesaid Example I series were used for ethylene homopolymerization or copolymerization under the following conditions according to the following processes respectively.

Homopolymerization: an autoclave for polymerization (5 L), a slurry polymerization process, hexane (2.5 L) as the solvent, a total polymerization pressure of 1.5 MPa, a polymerization temperature of 85° C., a ratio by molar of the co-catalyst to the active metal in the catalyst of 200, a polymerization time of 2 hours.

Specifically, 2.5 L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, 50 mg of a mixture of the supported nonmetallocene catalyst and the co-catalyst was added thereto, and ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 1.5 MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table I-1.

Copolymerization: an autoclave for polymerization (5 L), a slurry polymerization process, hexane (2.5 L) as the solvent, a total polymerization pressure of 1.5 MPa, a polymerization temperature of 85° C., a ratio by molar of the co-catalyst to the active metal in the catalyst of 200, a polymerization time of 2 hours.

Specifically, 2.5 L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, 50 mg of a mixture of the supported nonmetallocene catalyst and the co-catalyst was added thereto. Hexene-1 (50 g) was added thereto all at once as the comonomer. Ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 1.5 MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table I-1.

TABLE I-1

The results of the olefin polymerization obtained with the supported nonmetallocene catalysts

Experiment No.	Catalyst No.	Co-catalyst	type	Poly activity (kgPE/gCat)	Molecular weight distribution
1	CAT-I-1	methyl aluminoxane	homopolymerization	2.26	2.14
2	CAT-I-1	methyl aluminoxane	copolymerization	3.15	2.27
3	CAT-I-1	triethyl aluminum	homopolymerization	1.52	2.58
4	CAT-I-2	methyl aluminoxane	homopolymerization	2.73	2.20
5	CAT-I-3	methyl aluminoxane	homopolymerization	4.22	2.34
6	CAT-I-4	methyl aluminoxane	homopolymerization	2.65	2.20
7	CAT-I-5	methyl aluminoxane	homopolymerization	1.77	2.25
8	CAT-I-6	methyl aluminoxane	homopolymerization	1.50	2.16
9	CAT-I-7	methyl aluminoxane	homopolymerization	3.75	2.24
10	CAT-I-8	methyl aluminoxane	homopolymerization	1.65	2.16
11	CAT-I-9	methyl aluminoxane	homopolymerization	1.73	2.24
12	CAT-I-1-A	methyl aluminoxane	homopolymerization	3.75	2.10
13	CAT-I-1-B	methyl aluminoxane	homopolymerization	1.02	2.15
14	CAT-I-1-C	methyl aluminoxane	homopolymerization	2.02	2.14

As can be seen from the Table I-1, the polymer obtained from the polymerization by using the supported nonmetallocene catalyst produced in line with the present process exhibits a narrow molecular weight distribution. It is well known in this field that polyethylene produced from the polymerization by using a Ziegler-Natta catalyst usually exhibits a molecular weight distribution of about from 3 to 8.

Upon comparison of the results from the experiment No. 1 and those from the experiment Nos. 12 and 13 in the Table I-1, it is clear that the activity of the catalyst increases or decreases as the amount of the nonmetallocene complex to be introduced into the catalyst increases or decreases, while the molecular weight distribution of the polymer remains substantially unchanged. This fact indicates that the activity of the supported nonmetallocene catalyst of this invention originates from the nonmetallocene complex, and the performances of the polymer obtained from the polymerization depend on it as well.

Upon comparison of the results from the experiment No. 1 and those from the experiment No. 14 in the Table I-1, it is clear that the catalyst obtained by directing drying the slurry

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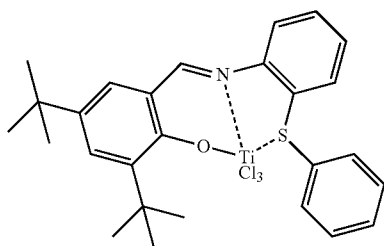
according to this invention exhibits a higher activity than that obtained by filtering and washing the slurry.

Example II

Corresponding to the Second Embodiment

Example II-1

Anhydrous magnesium chloride was used as the magnesium compound, tetrahydrofuran was used as the solvent for dissolving the magnesium compound and the nonmetallocene complex, silica gel (ES757, from the Ineos Company) was used as the porous carrier, the compound represented by



was used as the nonmetallocene complex.

The silica gel was thermally activated by continuously calcinating at 600° C. under a N₂ atmosphere for 4 hours before use.

5 g of the anhydrous magnesium chloride and the nonmetallocene complex were weighted, tetrahydrofuran was added thereto to completely dissolve same at the normal temperature. Then, the thermally activated silica gel was added thereto, after stirring for 2 hours, hexane (as the precipitating agent) was added thereto to precipitate same. The resultant solid was then filtered, washed by a solvent for washing (which is the same as the precipitating agent) for 2 times (by using the same amount as that of the precipitating agent each time) and then uniformly heated to 90° C. and vacuum dried, to obtain the supported nonmetallocene catalyst.

In this example, the ratio of magnesium chloride to tetrahydrofuran was 1 mol:210 ml, the ratio by molar of magnesium chloride to the nonmetallocene complex was 1:0.08, the ratio by weight of magnesium chloride to the porous carrier was 1:2, and the ratio by volume of the precipitating agent to tetrahydrofuran was 1:1.

The thus obtained supported nonmetallocene catalyst was named as CAT-II-1.

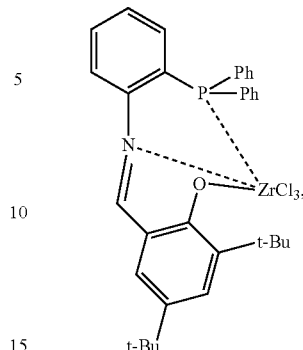
Example II-2

Substantially the same as the Example II-1, except for the following changes:

The porous carrier was changed to silica gel (955, from the Grace Company), which has been thermally activated by continuously calcinating at 400° C. under a N₂ gas atmosphere for 8 hours.

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The nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to toluene, and the precipitating agent was changed to cyclohexane.

In this example, the ratio of the magnesium compound to toluene was 1 mol:150 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.15, the ratio by weight of the magnesium compound to the porous carrier was 1:4, and the ratio by volume of the precipitating agent to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1:2.

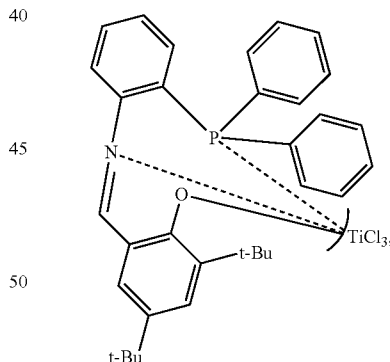
The thus obtained supported nonmetallocene catalyst was named as CAT-II-2.

Example II-3

Substantially the same as the Example II-1, except for the following changes:

The porous carrier was changed to Al₂O₃, which has been thermally activated by continuously calcinating at 700° C. under a N₂ gas atmosphere for 6 hours.

The magnesium compound was changed to anhydrous magnesium bromide (MgBr₂), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to ethyl benzene, and the precipitating agent was changed to cycloheptane.

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:250 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.20, the ratio by weight of the magnesium compound to the porous carrier was 1:1, and the ratio by volume of the precipitating agent to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1:0.80.

The thus obtained supported nonmetallocene catalyst was named as CAT-II-3.

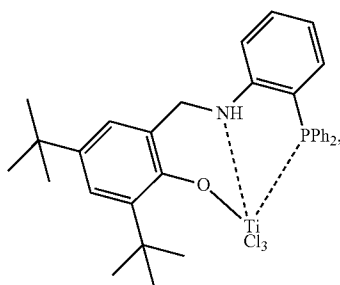
57

Example II-4

Substantially the same as the Example II-1, except for the following changes:

The porous carrier was changed to a mixed oxide of silica and MgO (at a ratio by weight of 1:1), which has been thermally activated by continuously calcinating at 600° C. under an Ar gas atmosphere for 4 hours.

The magnesium compound was changed to ethoxy magnesium chloride ($\text{MgCl}(\text{OC}_2\text{H}_5)$), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to xylene, and the precipitating agent was changed to decane.

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:300 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.04, the ratio by weight of the magnesium compound to the porous carrier was 1:3, and the ratio by volume of the precipitating agent to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1:2.

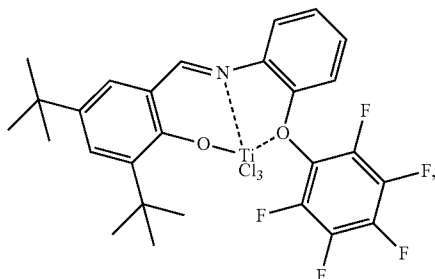
The thus obtained supported nonmetallocene catalyst was named as CAT-II-4.

Example II-5

Substantially the same as the Example II-1, except for the following changes:

The porous carrier was changed to montmorillonite, which has been thermally activated by continuously calcinating at 400° C. under a N₂ gas atmosphere for 8 hours.

The magnesium compound was changed to butoxy magnesium bromide ($\text{MgBr}(\text{OC}_4\text{H}_9)$), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to diethyl benzene.

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In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:400 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.30, and the ratio by weight of the magnesium compound to the porous carrier was 1:5.

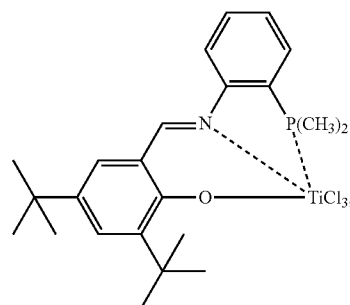
The thus obtained supported nonmetallocene catalyst was named as CAT-II-5.

Example II-6

Substantially the same as the Example II-1, except for the following changes:

The porous carrier was changed to polystyrene, which has been thermally activated by continuously drying at 85° C. under a N₂ gas atmosphere for 12 hours.

The magnesium compound was changed to methyl magnesium chloride ($\text{Mg}(\text{CH}_3)\text{Cl}$), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to chloro toluene.

In this example, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.10, the ratio by weight of the magnesium compound to the porous carrier was 1:10.

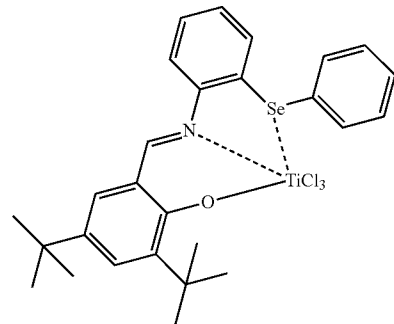
The thus obtained supported nonmetallocene catalyst was named as CAT-II-6.

Example II-7

Substantially the same as the Example II-1, except for the following changes:

The porous carrier was changed to kieselguhr, which has been thermally activated by continuously calcinating at 500° C. under a N₂ gas atmosphere for 8 hours.

The magnesium compound was changed to ethyl magnesium chloride ($\text{Mg}(\text{C}_2\text{H}_5)\text{Cl}$), the nonmetallocene complex was changed to



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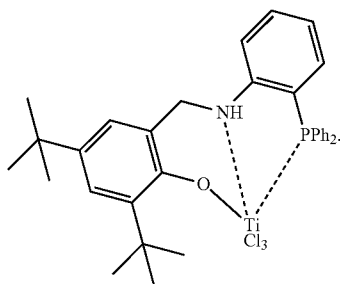
In this example, the ratio by weight of the magnesium compound to the porous carrier was 1:0.5.

The thus obtained supported nonmetallocene catalyst was named as CAT-II-7.

Example II-8

Substantially the same as the Example II-1, except for the following changes:

The magnesium compound was changed to ethyl magnesium ($\text{Mg}(\text{C}_2\text{H}_5)_2$), the nonmetallocene complex was changed to



The thus obtained supported nonmetallocene catalyst was named as CAT-II-8.

Example II-9

Substantially the same as the Example II-1, except for the following changes:

The magnesium compound was changed to methyl ethoxy magnesium ($\text{Mg}(\text{OC}_2\text{H}_5)(\text{CH}_3)$).

The thus obtained supported nonmetallocene catalyst was named as CAT-II-9.

Example II-10

Substantially the same as the Example II-1, except for the following changes:

The magnesium compound was changed to ethyl n-butoxy magnesium ($\text{Mg}(\text{OC}_4\text{H}_9)(\text{C}_2\text{H}_5)$).

The thus obtained supported nonmetallocene catalyst was named as CAT-II-10.

Reference Example II-1-A

Substantially the same as the Example II-1, except for the following changes:

The ratio by molar of magnesium chloride to the nonmetallocene complex was changed to 1:0.16.

The thus obtained catalyst was named as CAT-II-1-A.

Reference Example II-1-B

Substantially the same as the Example II-1, except for the following changes:

The ratio by molar of magnesium chloride to the nonmetallocene complex was changed to 1:0.04.

The thus obtained catalyst was named as CAT-II-1-B.

Application Example II

The catalysts CAT-II-1 to CAT-II-9, CAT-II-1-A to CAT-II-1-B obtained from the aforesaid Example II series were

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used for ethylene homopolymerization or copolymerization under the following conditions according to the following processes respectively.

Homopolymerization: an autoclave for polymerization (5 L), a slurry polymerization process, hexane (2.5 L) as the solvent, a total polymerization pressure of 1.5 MPa, a polymerization temperature of 85° C., a ratio by molar of the co-catalyst to the active metal in the catalyst of 200, a polymerization time of 2 hours.

Specifically, 2.5 L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, 50 mg of a mixture of the supported nonmetallocene catalyst and the co-catalyst was added thereto, and ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 1.5 MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table II-1.

Copolymerization: an autoclave for polymerization (5 L), a slurry polymerization process, hexane (2.5 L) as the solvent, a total polymerization pressure of 1.5 MPa, a polymerization temperature of 85° C., a ratio by molar of the co-catalyst to the active metal in the catalyst of 200, a polymerization time of 2 hours.

Specifically, 2.5 L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, 50 mg of a mixture of the supported nonmetallocene catalyst and the co-catalyst was added thereto. Hexene-1 (50 g) was added thereto all at once as the comonomer. Ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 1.5 MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table II-1.

TABLE II-1

The results of the olefin polymerization obtained with the supported nonmetallocene catalysts

Experiment No.	Catalyst No.	Co-catalyst	type	Poly activity (kgPE/gCat)	Molecular weight distribution
1	CAT-II-1	methyl aluminoxane	Homopolymerization	2.02	2.14
2	CAT-II-1	methyl aluminoxane	Copolymerization	3.03	2.27
3	CAT-II-1	triethyl aluminum	Homopolymerization	1.10	2.52
4	CAT-II-2	methyl aluminoxane	Homopolymerization	2.14	2.20
5	CAT-II-3	methyl aluminoxane	Homopolymerization	4.00	2.34
6	CAT-II-4	methyl aluminoxane	Homopolymerization	1.63	2.20
7	CAT-II-5	methyl aluminoxane	Homopolymerization	1.66	2.25
8	CAT-II-6	methyl aluminoxane	Homopolymerization	1.40	2.16
9	CAT-II-7	methyl aluminoxane	Homopolymerization	3.62	2.24
10	CAT-II-8	methyl aluminoxane	Homopolymerization	1.55	2.16

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TABLE II-1-continued

The results of the olefin polymerization obtained with the supported nonmetallocene catalysts					
Experiment No.	Catalyst No.	Co-catalyst	type	Poly activity (kgPE/gCat)	Molecular weight distribution
11	CAT-II-9	methylaluminoxane	Homopolymerization	1.69	2.24
12	CAT-II-1-A	methylaluminoxane	Homopolymerization	3.57	2.10
13	CAT-II-1-B	methylaluminoxane	Homopolymerization	0.99	2.15

As can be seen from the Table II-1, the polymer obtained from the polymerization by using the supported nonmetallocene catalyst produced in line with the present process exhibits a narrow molecular weight distribution. It is well known in this field that polyethylene produced from the polymerization by using a Ziegler-Natta catalyst usually exhibits a molecular weight distribution of about from 3 to 8.

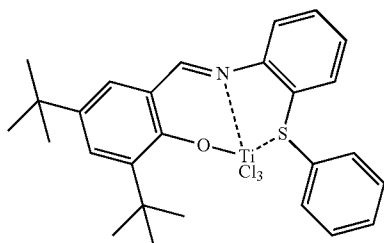
Upon comparison of the results from the experiment No. 1 and those from the experiment Nos. 12 and 13 in the Table II-1, it is clear that the activity of the catalyst increases or decreases as the amount of the nonmetallocene complex to be introduced into the catalyst increases or decreases, while the molecular weight distribution of the polymer remains substantially unchanged. This fact indicates that the activity of the supported nonmetallocene catalyst of this invention originates from the nonmetallocene complex, and the performances of the polymer obtained from the polymerization depend on it as well.

Example III

Corresponding to the Third Embodiment

Example III-1

Anhydrous magnesium chloride was used as the magnesium compound, tetrahydrofuran was used as the solvent for dissolving the magnesium compound and the nonmetallocene complex, titanium tetrachloride was used as the chemical treating agent, silica gel (ES757, from the Ineos Company) was used as the porous carrier, the compound represented by



was used as the nonmetallocene complex.

The silica gel was thermally activated by continuously calcinating at 600° C. under a N₂ atmosphere for 4 hours before use.

5 g of the anhydrous magnesium chloride and the nonmetallocene complex were weighted, tetrahydrofuran was added thereto to completely dissolve same at the normal temperature. Then, the thermally activated silica gel was added

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thereto, after stirring for 2 hours, the resultant was uniformly heated to 90° C. and directly vacuum dried, to obtain the composite carrier.

Then, to the composite carrier, 60 ml hexane was added, and then titanium tetrachloride was dropwise added thereto under stirring over a period of 30 minutes. The reaction continued at 60° C. under stirring for 4 hours, then filtered, washed with hexane for 2 times (60 ml each time), and vacuum dried at the normal temperature to obtain the supported nonmetallocene catalyst.

In this example, the ratio of magnesium chloride to tetrahydrofuran was 1 mol:210 ml, the ratio by molar of magnesium chloride to the nonmetallocene complex was 1:0.08, the ratio by weight of magnesium chloride to the porous carrier was 1:2, and the ratio by molar of magnesium chloride to titanium tetrachloride was 1:0.15.

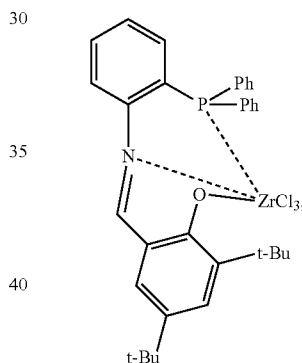
The thus obtained supported nonmetallocene catalyst was named as CAT-III-1.

Example III-1-1

Substantially the same as the Example III-1, except for the following changes:

The porous carrier was changed to silica gel (955, from the Grace Company), which has been thermally activated by continuously calcinating at 400° C. under a N₂ gas atmosphere for 8 hours.

The nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to toluene, and the chemical treating agent was changed to zirconium tetrachloride (ZrCl₄).

In this example, the ratio of the magnesium compound to toluene was 1 mol:150 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.15, the ratio by weight of the magnesium compound to the porous carrier was 1:4, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.20.

The thus obtained supported nonmetallocene catalyst was named as CAT-III-1-1.

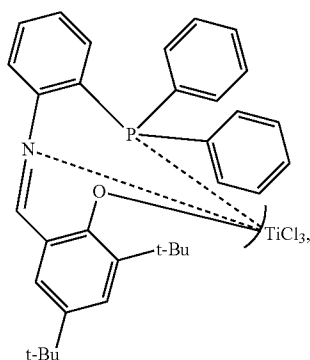
Example III-1-2

Substantially the same as the Example III-1, except for the following changes:

The porous carrier was changed to Al₂O₃, which has been thermally activated by continuously calcinating at 700° C. under a N₂ gas atmosphere for 6 hours.

The magnesium compound was changed to anhydrous magnesium bromide (MgBr₂), the nonmetallocene complex was changed to

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the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to ethyl benzene, and the chemical treating agent was changed to titanium tetrabromide (TiBr_4).

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:250 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.2, the ratio by weight of the magnesium compound to the porous carrier was 1:1, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.30.

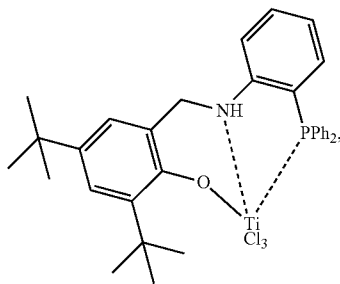
The thus obtained supported nonmetallocene catalyst was named as CAT-III-1-2.

Example III-1-3

Substantially the same as the Example III-1, except for the following changes:

The porous carrier was changed to a mixed oxide of silica and MgO (at a ratio by weight of 1:1), which has been thermally activated by continuously calcinating at 600°C . under an Ar gas atmosphere for 4 hours.

The magnesium compound was changed to ethoxy magnesium chloride ($\text{MgCl}(\text{OC}_2\text{H}_5)$), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to xylene, and the chemical treating agent was changed to tetraethyl titanium ($\text{Ti}(\text{CH}_3\text{CH}_2)_4$).

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:300 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.04, and the ratio by weight of the magnesium compound to the porous carrier was 1:3, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.05.

The thus obtained supported nonmetallocene catalyst was named as CAT-III-1-3.

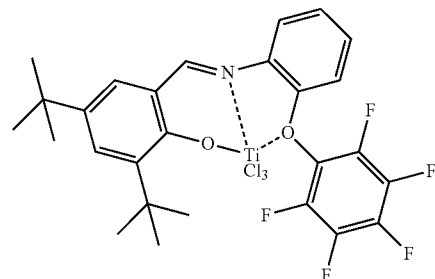
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Example III-1-4

Substantially the same as the Example III-1, except for the following changes:

The porous carrier was changed to montmorillonite, which has been thermally activated by continuously calcinating at 400°C . under a N_2 gas atmosphere for 8 hours.

The magnesium compound was changed to butoxy magnesium bromide ($\text{MgBr}(\text{OC}_4\text{H}_9)$), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to diethyl benzene, and the chemical treating agent was changed to tetran-butyl titanium ($\text{Ti}(\text{C}_4\text{H}_9)_4$).

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:400 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.30, the ratio by weight of the magnesium compound to the porous carrier was 1:5, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.50.

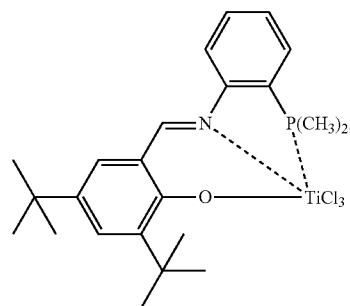
The thus obtained supported nonmetallocene catalyst was named as CAT-III-4.

Example III-1-5

Substantially the same as the Example III-1, except for the following changes:

The porous carrier was changed to polystyrene, which has been thermally activated by continuously drying at 85°C . under a N_2 gas atmosphere for 12 hours.

The magnesium compound was changed to methyl magnesium chloride ($\text{Mg}(\text{CH}_3)\text{Cl}$), the nonmetallocene complex was changed to



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the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to chloro toluene, and the chemical treating agent was changed to tetraethyl zirconium ($\text{Zr}(\text{CH}_3\text{CH}_2)_4$).

In this example, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.10, the ratio by weight of the magnesium compound to the porous carrier was 1:10, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.10.

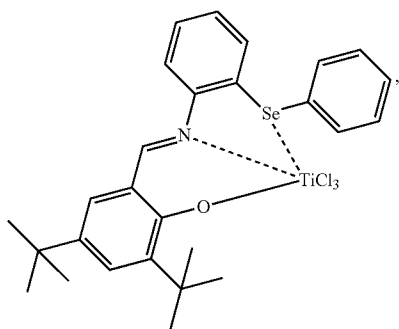
The thus obtained supported nonmetallocene catalyst was named as CAT-III-1-5.

Example III-1-6

Substantially the same as the Example III-1, except for the following changes:

The porous carrier was changed to kieselguhr, which has been thermally activated by continuously calcinating at 500° C. under a N_2 gas atmosphere for 8 hours.

The magnesium compound was changed to ethyl magnesium chloride ($\text{Mg}(\text{C}_2\text{H}_5)\text{Cl}$), the nonmetallocene complex was changed to



and the chemical treating agent was changed to tetraethoxy titanium ($\text{Ti}(\text{OCH}_3\text{CH}_2)_4$).

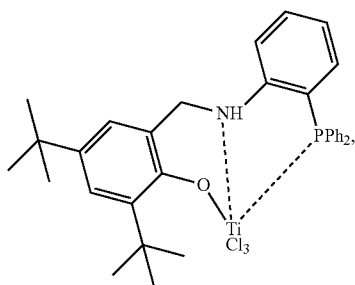
In this example, the ratio by weight of the magnesium compound to the porous carrier was 1:0.5.

The thus obtained supported nonmetallocene catalyst was named as CAT-III-1-6.

Example III-1-7

Substantially the same as the Example III-1, except for the following changes:

The magnesium compound was changed to ethyl magnesium ($\text{Mg}(\text{C}_2\text{H}_5)_2$), the nonmetallocene complex was changed to



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and the chemical treating agent was changed to isobutyl trichloro titanium ($\text{Ti}(\text{i-C}_4\text{H}_9)\text{Cl}_3$).

The thus obtained supported nonmetallocene catalyst was named as CAT-III-1-7.

Example III-1-8

Substantially the same as the Example III-1, except for the following changes:

The magnesium compound was changed to methyl ethoxy magnesium ($\text{Mg}(\text{OC}_2\text{H}_5)(\text{CH}_3)$), and the chemical treating agent was changed to triisobutoxy chloro titanium ($\text{TiCl}(\text{i-OC}_4\text{H}_9)_3$).

The thus obtained supported nonmetallocene catalyst was named as CAT-III-1-8.

Example III-1-9

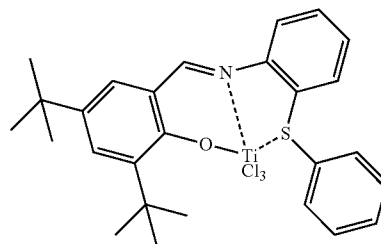
Substantially the same as the Example III-1, except for the following changes:

The magnesium compound was changed to ethyl n-butoxy magnesium ($\text{Mg}(\text{OC}_4\text{H}_9)(\text{C}_2\text{H}_5)$), and the chemical treating agent was changed to dimethoxy dichloro zirconium ($\text{ZrCl}_2(\text{OCH}_3)_2$).

The thus obtained supported nonmetallocene catalyst was named as CAT-III-1-9.

Example III-2

Anhydrous magnesium chloride was used as the magnesium compound, tetrahydrofuran was used as the solvent for dissolving the magnesium compound and the nonmetallocene complex, titanium tetrachloride was used as the chemical treating agent, silica gel (ES757, from the Ineos Company) was used as the porous carrier, the compound represented by



was used as the nonmetallocene complex.

The silica gel was thermally activated by continuously calcinating at 600° C. under a N_2 atmosphere for 4 hours before use.

5 g of the anhydrous magnesium chloride and the nonmetallocene complex were weighted, tetrahydrofuran was added thereto to completely dissolve same at the normal temperature. Then, the thermally activated silica gel was added thereto, after stirring for 2 hours, the resultant was uniformly heated to 90° C. and directly vacuum dried, to obtain the composite carrier.

Then, to the composite carrier, 60 ml hexane was added, and then triethyl aluminum (as the assistant chemical treating agent, at a concentration of 15 wt % in hexane) was dropwise added thereto under stirring over a period of 30 minutes. The reaction continued at 60° C. under stirring for 4 hours, then filtered, washed with hexane for 2 times (60 ml each time), and vacuum dried at the normal temperature.

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Then, to the thus pre-treated composite carrier, 60 ml hexane was added, and then titanium tetrachloride was dropwise added thereto under stirring over a period of 30 minutes. The reaction continued at 60° C. under stirring for 4 hours, then filtered, washed with hexane for 2 times (60 ml each time), and vacuum dried at the normal temperature to obtain the supported nonmetallocene catalyst.

In this example, the ratio of magnesium chloride to tetrahydrofuran was 1 mol:210 ml, the ratio by molar of magnesium chloride to the nonmetallocene complex was 1:0.08, the ratio by weight of magnesium chloride to the porous carrier was 1:2, the ratio by molar of magnesium chloride to triethyl aluminum was 1:0.15, and the ratio by molar of magnesium chloride to titanium tetrachloride was 1:0.15.

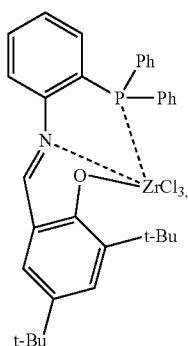
The thus obtained supported nonmetallocene catalyst was named as CAT-III-2.

Example III-2-1

Substantially the same as the Example III-2, except for the following changes:

The porous carrier was changed to silica gel (955, from the Grace Company), which has been thermally activated by continuously calcinating at 400° C. under a N₂ gas atmosphere for 8 hours.

The nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to toluene, the assistant chemical treating agent was changed to methyl aluminumoxane (MAO, a 10 wt % solution in toluene), and the chemical treating agent was changed to zirconium tetrachloride (ZrCl₄).

After pre-treated with the assistant chemical treating agent, the resultant was washed with toluene for 3 times.

In this example, the ratio of the magnesium compound to toluene was 1 mol:150 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.15, the ratio by weight of the magnesium compound to the porous carrier was 1:4, the ratio by molar of the magnesium compound to the assistant chemical treating agent was 1:0.15, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.20.

The thus obtained supported nonmetallocene catalyst was named as CAT-III-2-1.

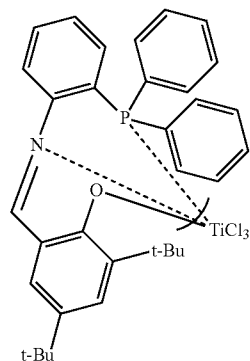
Example III-2-2

Substantially the same as the Example III-2, except for the following changes:

The porous carrier was changed to Al₂O₃, which has been thermally activated by continuously calcinating at 700° C. under a N₂ gas atmosphere for 6 hours.

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The magnesium compound was changed to anhydrous magnesium bromide (MgBr₂), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to ethyl benzene, the assistant chemical treating agent was changed to trimethyl aluminum (Al(CH₃)₃), and the chemical treating agent was changed to titanium tetrabromide (TiBr₄).

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:250 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.2, the ratio by weight of the magnesium compound to the porous carrier was 1:1, the ratio by molar of the magnesium compound to the assistant chemical treating agent was 1:0.30, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.30.

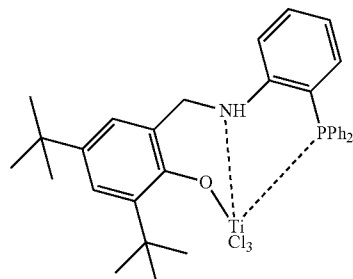
The thus obtained supported nonmetallocene catalyst was named as CAT-III-2-2.

Example III-2-3

Substantially the same as the Example III-2, except for the following changes:

The porous carrier was changed to a mixed oxide of silica and MgO (at a ratio by weight of 1:1), which has been thermally activated by continuously calcinating at 600° C. under an Ar gas atmosphere for 4 hours.

The magnesium compound was changed to ethoxy magnesium chloride (MgCl(OC₂H₅)), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to xylene, the assistant

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chemical treating agent was changed to triisobutyl aluminum ($\text{Al}(\text{i-C}_4\text{H}_9)_3$), and the chemical treating agent was changed to tetraethyl titanium ($\text{Ti}(\text{CH}_3\text{CH}_2)_4$).

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:300 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.04, and the ratio by weight of the magnesium compound to the porous carrier was 1:3, the ratio by molar of the magnesium compound to the assistant chemical treating agent was 1:0.05, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.05.

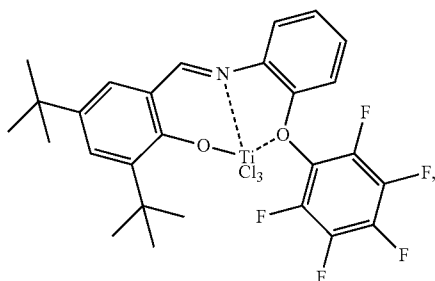
The thus obtained supported nonmetallocene catalyst was named as CAT-III-2-3.

Example III-2-4

Substantially the same as the Example III-2, except for the following changes:

The porous carrier was changed to montmorillonite, which has been thermally activated by continuously calcinating at 400° C. under a N_2 gas atmosphere for 8 hours.

The magnesium compound was changed to butoxy magnesium bromide ($\text{MgBr}(\text{OC}_4\text{H}_9)$), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to diethyl benzene, the assistant chemical treating agent was changed to isobutyl aluminoxane, and the chemical treating agent was changed to tetran-butyl titanium ($\text{Ti}(\text{C}_4\text{H}_9)_4$).

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:400 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.30, the ratio by weight of the magnesium compound to the porous carrier was 1:5, the ratio by molar of the magnesium compound to the assistant chemical treating agent was 1:0.50, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.50.

The thus obtained supported nonmetallocene catalyst was named as CAT-III-2-4.

Example III-2-5

Substantially the same as the Example III-2, except for the following changes:

The porous carrier was changed to polystyrene, which has been thermally activated by continuously drying at 85° C. under a N_2 gas atmosphere for 12 hours.

The magnesium compound was changed to methyl magnesium chloride ($\text{Mg}(\text{CH}_3)\text{Cl}$), the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to chloro toluene, the assistant chemical treating

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agent was changed to diethyl methyl aluminum ($\text{Al}(\text{CH}_3)(\text{CH}_3\text{CH}_2)_2$), and the chemical treating agent was changed to tetraethyl zirconium ($\text{Zr}(\text{CH}_3\text{CH}_2)_4$).

In this example, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.10, the ratio by weight of the magnesium compound to the porous carrier was 1:10, the ratio by molar of the magnesium compound to the assistant chemical treating agent was 1:0.10, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.10.

The thus obtained supported nonmetallocene catalyst was named as CAT-III-2-5.

Reference Example III-1-A

Substantially the same as the Example III-1, except for the following changes:

No nonmetallocene complex was used.

The thus obtained catalyst was named as CAT-III-1-A.

Reference Example III-1-B

Substantially the same as the Example III-1, except for the following changes:

The ratio by molar of magnesium chloride to the nonmetallocene complex was changed to 1:0.16.

The thus obtained catalyst was named as CAT-III-1-B.

Reference Example III-1-C

Substantially the same as the Example III-1, except for the following changes:

The ratio by molar of magnesium chloride to the nonmetallocene complex was changed to 1:0.04.

The thus obtained catalyst was named as CAT-III-1-C.

Reference Example III-1-D

Substantially the same as the Example III-1, except for the following changes:

The composite carrier was not treated by titanium tetrachloride.

The thus obtained catalyst was named as CAT-III-1-D.

Reference Example III-1-E

Substantially the same as the Example III-1, except for the following changes:

In preparation of the composite carrier, 60 ml hexane was added to the slurry to precipitate same, which was then filtered, washed with hexane for 3 times (60 ml per time), and finally vacuum dried at 60° C.

The thus obtained catalyst was named as CAT-III-1-E.

Example III-3

Application Example

The catalysts CAT-III-1, CAT-II-2, CAT-III-1-1 to CAT-III-1-5, CAT-III-2-5, CAT-III-1-A to CAT-III-1-E obtained from the aforesaid Example III series were used for ethylene homopolymerization/copolymerization and ultra high molecular weight polyethylene preparation under the following conditions according to the following processes respectively.

Homopolymerization: an autoclave for polymerization (5 L), a slurry polymerization process, hexane (2.5 L) as the

solvent, a total polymerization pressure of 0.8 MPa, a polymerization temperature of 85° C., a partial pressure of hydrogen gas of 0.2 MPa, a polymerization time of 2 hours.

Specifically, 2.5 L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, 50 mg of a mixture of the supported nonmetallocene catalyst and the co-catalyst was added thereto, and then hydrogen gas was supplied thereto till 0.2 MPa, and finally ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 0.8 MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table III-1.

Copolymerization: an autoclave for polymerization (5 L), a slurry polymerization process, hexane (2.5 L) as the solvent, a total polymerization pressure of 0.8 MPa, a polymerization temperature of 85° C., a partial pressure of hydrogen gas of 0.2 MPa, a polymerization time of 2 hours.

Specifically, 2.5 L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, 50 mg of a mixture of the supported nonmetallocene catalyst and the co-catalyst was added thereto. Hexene-1 (50 g) was added thereto all at once as the comonomer, and then hydrogen gas

was supplied thereto till 0.2 MPa, and finally ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 0.8 MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table III-1.

Preparation of ultra high molecular weight polyethylene: an autoclave for polymerization (5 L), a slurry polymerization process, hexane (2.5 L) as the solvent, a total polymerization pressure of 0.5 MPa, a polymerization temperature of 70° C., a ratio by molar of the co-catalyst to the active metal in the catalyst of 100, a polymerization time of 6 hours.

Specifically, 2.5 L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, 50 mg of a mixture of the supported nonmetallocene catalyst and the co-catalyst was added thereto, and finally ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 0.5 MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table III-2.

TABLE III-1

The results of the olefin polymerization obtained with the supported nonmetallocene catalysts							
Experiment No.	Catalyst No.	Co-catalyst	ratio by molar of co-catalyst to active metal	type	Poly activity (kgPE/gCat)	Bulk density (g/cm ³)	Molecular weight distribution
1	CAT-III-1	triethyl aluminum	100	homopolymerization	6.30	0.31	3.13
2	CAT-III-1	methyl aluminumoxane	100	homopolymerization	4.15	0.33	2.75
3	CAT-III-1	triethyl aluminum	100	copolymerization	8.36	0.33	3.34
4	CAT-III-1	triethyl aluminum	500	copolymerization	8.61	0.33	3.22
5	CAT-III-1-1	triethyl aluminum	100	homopolymerization	2.74	0.26	—
6	CAT-III-1-2	triethyl aluminum	100	homopolymerization	6.54	0.29	—
7	CAT-III-1-3	triethyl aluminum	100	homopolymerization	3.06	0.27	—
8	CAT-III-1-4	triethyl aluminum	100	homopolymerization	2.16	0.26	—
9	CAT-III-1-5	triethyl aluminum	100	homopolymerization	2.47	0.30	—
10	CAT-III-2	triethyl aluminum	100	homopolymerization	7.17	0.33	2.94
11	CAT-III-2	methyl aluminumoxane	100	homopolymerization	4.64	0.35	2.67
12	CAT-III-2	triethyl aluminum	100	copolymerization	8.82	0.32	3.20
13	CAT-III-2-1	triethyl aluminum	100	homopolymerization	3.16	0.27	—
14	CAT-III-2-2	triethyl aluminum	100	homopolymerization	5.07	0.30	—
15	CAT-III-2-3	triethyl aluminum	100	homopolymerization	3.55	0.29	—
16	CAT-III-2-4	triethyl aluminum	100	homopolymerization	2.68	0.28	—
17	CAT-III-2-5	triethyl aluminum	100	homopolymerization	6.11	0.31	—
18	CAT-III-1-A	triethyl aluminum	100	homopolymerization	4.77	0.30	4.75
19	CAT-III-1-B	triethyl aluminum	100	homopolymerization	7.44	0.34	2.84
20	CAT-III-1-C	triethyl aluminum	100	homopolymerization	5.19	0.31	3.76

TABLE III-1-continued

The results of the olefin polymerization obtained with the supported nonmetallocene catalysts							
Experiment No.	Catalyst No.	Co-catalyst	ratio by molar of co-catalyst to active metal	type	Poly activity (kgPE/gCat)	Bulk density (g/cm ³)	Molecular weight distribution
21	CAT-III-1-D	triethyl aluminum	100	homopolymerization	1.52	0.26	2.58
22	CAT-III-1-E	triethyl aluminum	100	homopolymerization	5.83	0.31	3.04

TABLE III-2

The results of the ultra high molecular weight polyethylene preparation obtained with the supported nonmetallocene catalysts					
Experiment No.	Catalyst No.	Co-catalyst	Poly activity (kgPE/gCat)	Bulk density (g/cm ³)	Mv (10 ⁴ g/mol)
1	CAT-III-1	triethyl aluminum	8.84	0.36	420
2	CAT-III-1	methyl aluminumoxane	6.32	0.38	475
3	CAT-III-2	triethyl aluminum	10.41	0.37	450
4	CAT-III-2	methyl aluminumoxane	9.45	0.39	522
5	CAT-III-1-A	triethyl aluminum	5.44	0.33	294
6	CAT-III-1-B	triethyl aluminum	9.77	0.35	480
7	CAT-III-1-C	triethyl aluminum	6.25	0.35	365
8	CAT-III-1-D	triethyl aluminum	2.92	0.27	575
9	CAT-III-1-E	triethyl aluminum	8.27	0.36	440

As can be seen from the results of the experiment Nos. 3 and 4 in the Table III-1, increasing the amount of the co-catalyst to be used (i.e. increasing the ratio by molar of the co-catalyst to the active metal in the catalyst) will not significantly change the polymerization activity and the bulk density of the polymer. This fact indicates that a high activity for olefin polymerization can be obtained with a relatively less amount of the co-catalyst when the supported nonmetallocene catalyst produced in line with the process of this invention is used herein, and the resultant polymer product (for example polyethylene) exhibits superior polymer morphology and a high polymer bulk density.

Upon comparison of the results of the experiment No. 1 and those of the experiment No. 3, the results of the experiment No. 10 and those of the experiment No. 12, in the Table III-1, it is clear that in case of copolymerization, the polymerization activity increases significantly. This fact indicates that the supported nonmetallocene catalyst produced in line with the process of this invention exhibits a relatively significant co-monomer effect.

Upon comparison of the results from the experiment No. 1 and those from the reference example experiment Nos. 18 to 21 in the Table III-1, it is clear that the activity of the catalyst increases or decreases as the amount of the nonmetallocene complex to be introduced into the catalyst increases or decreases, while the molecular weight distribution of the

polymer narrows or broadens accordingly. Further, the activity of the catalyst increases or decreases as the amount of the chemical treating agent to be introduced into the catalyst increases or decreases, while the molecular weight distribution of the polymer broadens or narrows accordingly. This fact indicates that the nonmetallocene complex shows a function of narrowing the molecular weight distribution of the polymer, while the chemical treating agent shows a function of increasing the activity of the catalyst and broadening the molecular weight distribution of the polymer. For this reason, different catalysts in terms of activity and polymer performances can be obtained with this invention by altering the ratio between these two components.

As can be seen from the Table III-2, it is possible to prepare an ultra high molecular weight polyethylene (with to some degree increased bulk density) by using the catalyst according to this invention. Upon comparison of the results from the experiment No. 1 and those from the experiment No. 2, the results from the experiment No. 3 and those from the experiment No. 4, it is clear that the viscosity averaged molecular weight of the polymer can be increased by using MAO as the co-catalyst. Upon comparison of the results from the experiment No. 1 and those from the reference example experiment Nos. 5 to 8 in the Table III-2, it is clear that the viscosity averaged molecular weight of the polymer increases or decreases as the amount of the nonmetallocene complex to be introduced into the catalyst increases or decreases. This fact indicates that the nonmetallocene complex further shows a function of increasing the viscosity averaged molecular weight of the polymer.

As can be seen from the results of the experiment Nos. 1, 18 and 21 in the Table III-1 and those of the experiment Nos. 1, 5 and 8 in the Table III-2, the catalyst obtained with the case wherein only nonmetallocene complex was used in preparation of the supported nonmetallocene catalyst, or that obtained with the case wherein only chemical treating agent was used in preparation of the supported nonmetallocene catalyst, shows lowered activity than that obtained with the case wherein both of the nonmetallocene complex and the chemical treating agent were used in preparation of the supported nonmetallocene catalyst. This fact indicates that the supported nonmetallocene catalyst produced in line with the process of this invention necessarily involves a synergic effect. That is, the activity observed with the case wherein both components exist is higher than that observed with the case wherein only either component exists.

Upon comparison of the results from the experiment No. 1 and those from the experiment No. 22 in the Table III-1, and the results of the experiment No. 1 and those from the experiment No. 9 in the Table III-2, it is clear that the catalyst obtained by directing drying the slurry exhibits a higher activity than that obtained by filtering and washing the slurry.

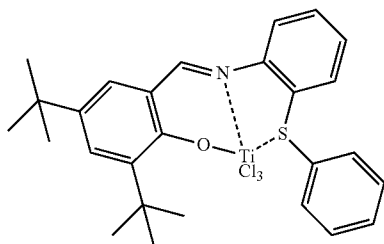
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Example IV

Corresponding to the Fourth Embodiment

Example IV-1

Anhydrous magnesium chloride was used as the magnesium compound, tetrahydrofuran was used as the solvent for dissolving the magnesium compound and the nonmetallocene complex, titanium tetrachloride was used as the chemical treating agent, silica gel (ES757, from the Ineos Company) was used as the porous carrier, the compound represented by



was used as the nonmetallocene complex.

The silica gel was thermally activated by continuously calcinating at 600° C. under a N₂ atmosphere for 4 hours before use.

5 g of the anhydrous magnesium chloride and the nonmetallocene complex were weighted, tetrahydrofuran was added thereto to completely dissolve same at the normal temperature. Then, the thermally activated silica gel was added thereto, after stirring for 2 hours, hexane (as the precipitating agent) was added thereto to precipitate same. The resultant solid was then filtered, washed by a solvent for washing (which is the same as the precipitating agent) for 2 times (by using the same amount as that of the precipitating agent each time) and then uniformly heated to 60° C. and vacuum dried, to obtain the composite carrier.

Then, to the composite carrier, 60 ml hexane was added, and then titanium tetrachloride was dropwise added thereto under stirring over a period of 30 minutes. The reaction continued at 60° C. under stirring for 4 hours, then filtered, washed with hexane for 2 times (60 ml each time), and vacuum dried at the normal temperature to obtain the supported nonmetallocene catalyst.

In this example, the ratio of magnesium chloride to tetrahydrofuran was 1 mol:210 ml, the ratio by molar of magnesium chloride to the nonmetallocene complex was 1:0.07, the ratio by weight of magnesium chloride to the porous carrier was 1:2, the ratio by volume of the precipitating agent to tetrahydrofuran was 1:1, and the ratio by molar of magnesium chloride to titanium tetrachloride was 1:0.15.

The thus obtained supported nonmetallocene catalyst was named as CAT-IV-1.

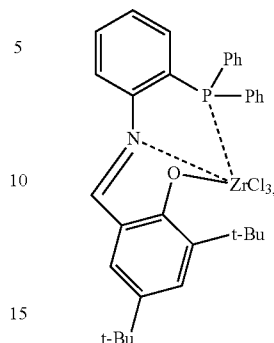
Example IV-1-1

Substantially the same as the Example IV-1, except for the following changes:

The porous carrier was changed to silica gel (955, from the Grace Company), which has been thermally activated by continuously calcinating at 400° C. under a N₂ gas atmosphere for 8 hours.

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The nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to toluene, the precipitating agent was changed to cyclohexane, and the chemical treating agent was changed to zirconium tetrachloride (ZrCl₄).

In this example, the ratio of the magnesium compound to toluene was 1 mol:150 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.15, the ratio by weight of the magnesium compound to the porous carrier was 1:4, the ratio by volume of the precipitating agent to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1:2, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.20.

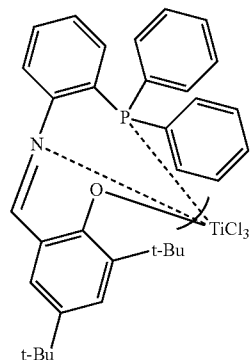
The thus obtained supported nonmetallocene catalyst was named as CAT-IV-1-1.

Example IV-1-2

Substantially the same as the Example IV-1, except for the following changes:

The porous carrier was changed to Al₂O₃, which has been thermally activated by continuously calcinating at 700° C. under a N₂ gas atmosphere for 6 hours.

The magnesium compound was changed to anhydrous magnesium bromide (MgBr₂), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to ethyl benzene, the precipitating agent was changed to cycloheptane, and the chemical treating agent was changed to titanium tetrabromide (TiBr₄).

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the

The thus obtained supported nonmetallocene catalyst was named as CAT-IV-1-5.

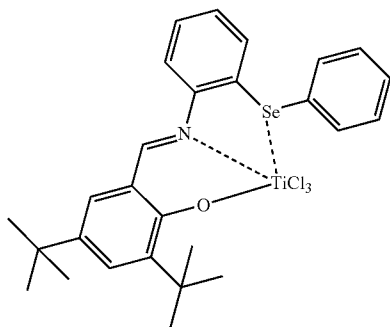
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Example IV-1-6

Substantially the same as the Example IV-1, except for the following changes:

The porous carrier was changed to kieselguhr, which has been thermally activated by continuously calcinating at 500° C. under a N₂ gas atmosphere for 8 hours.

The magnesium compound was changed to ethyl magnesium chloride (Mg(C₂H₅)Cl), the nonmetallocene complex was changed to



and the chemical treating agent was changed to tetraethoxy titanium (Ti(OCH₂CH₃)₄).

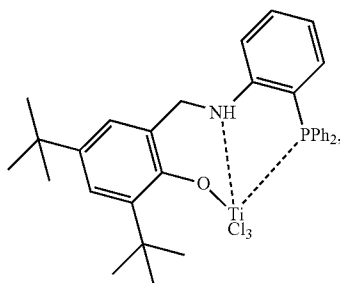
In this example, the ratio by weight of the magnesium compound to the porous carrier was 1:0.5.

The thus obtained supported nonmetallocene catalyst was named as CAT-IV-1-6.

Example IV-1-7

Substantially the same as the Example IV-1, except for the following changes:

The magnesium compound was changed to ethyl magnesium (Mg(C₂H₅)₂), the nonmetallocene complex was changed to



and the chemical treating agent was changed to isobutyl trichloro titanium (Ti(i-C₄H₉)Cl₃).

The thus obtained supported nonmetallocene catalyst was named as CAT-IV-1-7.

Example IV-1-8

Substantially the same as the Example IV-1, except for the following changes:

The magnesium compound was changed to methyl ethoxy magnesium (Mg(OC₂H₅)(CH₃)), and the chemical treating agent was changed to triisobutoxy chloro titanium (TiCl(i-C₄H₉)₃).

The thus obtained supported nonmetallocene catalyst was named as CAT-IV-1-8.

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Example IV-1-9

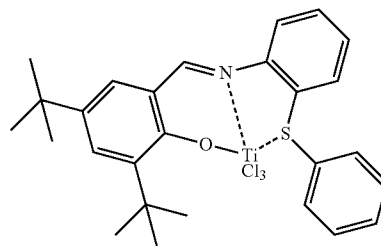
Substantially the same as the Example IV-1, except for the following changes:

The magnesium compound was changed to ethyl n-butoxy magnesium (Mg(OC₄H₉)(C₂H₅)), and the chemical treating agent was changed to dimethoxy dichloro zirconium (ZrCl₂(OCH₃)₂).

The thus obtained supported nonmetallocene catalyst was named as CAT-IV-1-9.

Example IV-2

Anhydrous magnesium chloride was used as the magnesium compound, tetrahydrofuran was used as the solvent for dissolving the magnesium compound and the nonmetallocene complex, titanium tetrachloride was used as the chemical treating agent, silica gel (ES757, from the Ineos Company) was used as the porous carrier, the compound represented by



was used as the nonmetallocene complex.

The silica gel was thermally activated by continuously calcinating at 600° C. under a N₂ atmosphere for 4 hours before use.

5 g of the anhydrous magnesium chloride and the nonmetallocene complex were weighted, tetrahydrofuran was added thereto to completely dissolve same at the normal temperature. Then, the thermally activated silica gel was added thereto, after stirring for 2 hours, hexane (as the precipitating agent) was added thereto to precipitate same. The resultant solid was then filtered, washed by a solvent for washing (which is the same as the precipitating agent) for 2 times (by using the same amount as that of the precipitating agent each time) and then uniformly heated to 60° C. and vacuum dried, to obtain the composite carrier.

Then, to the composite carrier, 60 ml hexane was added, and then triethyl aluminum (as the assistant chemical treating agent, at a concentration of 15 wt % in hexane) was dropwise added thereto under stirring over a period of 30 minutes. The reaction continued at 60° C. under stirring for 4 hours, then filtered, washed with hexane for 2 times (60 ml each time), and vacuum dried at the normal temperature.

Then, to the thus pre-treated composite carrier, 60 ml hexane was added, and then titanium tetrachloride was dropwise added thereto under stirring over a period of 30 minutes. The reaction continued at 60° C. under stirring for 4 hours, then filtered, washed with hexane for 2 times (60 ml each time), and vacuum dried at the normal temperature to obtain the supported nonmetallocene catalyst.

In this example, the ratio of magnesium chloride to tetrahydrofuran was 1 mol:210 ml, the ratio by molar of magnesium

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chloride to the nonmetallocene complex was 1:0.07, the ratio by weight of magnesium chloride to the porous carrier was 1:2, the ratio by volume of the precipitating agent to tetrahydrofuran was 1:1, the ratio by molar of magnesium chloride to triethyl aluminum was 1:0.15, and the ratio by molar of magnesium chloride to titanium tetrachloride was 1:0.15.

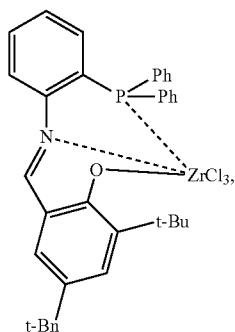
The thus obtained supported nonmetallocene catalyst was named as CAT-IV-2.

Example IV-2-1

Substantially the same as the Example IV-2, except for the following changes:

The porous carrier was changed to silica gel (955, from the Grace Company), which has been thermally activated by continuously calcinating at 400° C. under a N₂ gas atmosphere for 8 hours.

The nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to toluene, the precipitating agent was changed to cyclohexane, the assistant chemical treating agent was changed to methyl aluminoxane (MAO, a 10 wt % solution in toluene), and the chemical treating agent was changed to zirconium tetrachloride (ZrCl₄).

After pre-treated with the assistant chemical treating agent, the resultant was washed with toluene for 3 times.

In this example, the ratio of the magnesium compound to toluene was 1 mol:150 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.15, the ratio by weight of the magnesium compound to the porous carrier was 1:4, the ratio by volume of the precipitating agent to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1:2, the ratio by molar of the magnesium compound to the assistant chemical treating agent was 1:0.15, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.20.

The thus obtained supported nonmetallocene catalyst was named as CAT-IV-2-1.

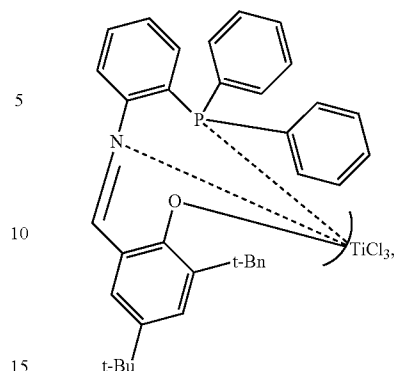
Example IV-2-2

Substantially the same as the Example IV-2, except for the following changes:

The porous carrier was changed to Al₂O₃, which has been thermally activated by continuously calcinating at 700° C. under a N₂ gas atmosphere for 6 hours.

The magnesium compound was changed to anhydrous magnesium bromide (MgBr₂), the nonmetallocene complex was changed to

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the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to ethyl benzene, the precipitating agent was changed to cycloheptane, the assistant chemical treating agent was changed to trimethyl aluminum (Al(CH₃)₃), and the chemical treating agent was changed to titanium tetrabromide (TiBr₄).

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:250 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.2, the ratio by weight of the magnesium compound to the porous carrier was 1:1, the ratio by volume of the precipitating agent to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1:0.70, the ratio by molar of the magnesium compound to the assistant chemical treating agent was 1:0.30, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.30.

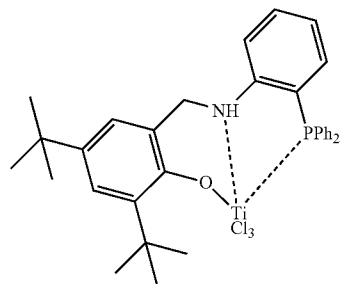
The thus obtained supported nonmetallocene catalyst was named as CAT-IV-2-2.

Example IV-2-3

Substantially the same as the Example IV-2, except for the following changes:

The porous carrier was changed to a mixed oxide of silica and MgO (at a ratio by weight of 1:1), which has been thermally activated by continuously calcinating at 600° C. under an Ar gas atmosphere for 4 hours.

The magnesium compound was changed to ethoxy magnesium chloride (MgCl(OC₂H₅)), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to xylene, the precipitating agent was changed to decane, the assistant chemical treating agent was changed to triisobutyl aluminum (Al(i-

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$C_4H_9)_3$), and the chemical treating agent was changed to tetraethyl titanium ($Ti(CH_3CH_2)_4$).

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:300 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.04, and the ratio by weight of the magnesium compound to the porous carrier was 1:3, the ratio by volume of the precipitating agent to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1:1.5, the ratio by molar of the magnesium compound to the assistant chemical treating agent was 1:0.05, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.05.

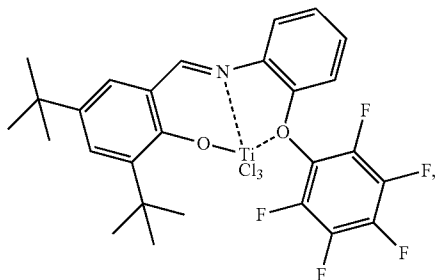
The thus obtained supported nonmetallocene catalyst was named as CAT-IV-2-3.

Example IV-2-4

Substantially the same as the Example IV-2, except for the following changes:

The porous carrier was changed to montmorillonite, which has been thermally activated by continuously calcinating at 400° C. under a N_2 gas atmosphere for 8 hours.

The magnesium compound was changed to butoxy magnesium bromide ($MgBr(OC_4H_9)$), the nonmetallocene complex was changed to



the solvent for dissolving the magnesium compound and the nonmetallocene complex was changed to diethyl benzene, the assistant chemical treating agent was changed to isobutyl aluminoxane, and the chemical treating agent was changed to tetran-butyl titanium ($Ti(C_4H_9)_4$).

In this example, the ratio of the magnesium compound to the solvent for dissolving the magnesium compound and the nonmetallocene complex was 1 mol:400 ml, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.30, the ratio by weight of the magnesium compound to the porous carrier was 1:5, the ratio by molar of the magnesium compound to the assistant chemical treating agent was 1:0.50, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.50.

The thus obtained supported nonmetallocene catalyst was named as CAT-IV-2-4.

Example IV-2-5

Substantially the same as the Example IV-2, except for the following changes:

The porous carrier was changed to polystyrene, which has been thermally activated by continuously drying at 85° C. under a N_2 gas atmosphere for 12 hours.

The magnesium compound was changed to methyl magnesium chloride ($Mg(CH_3)Cl$), the solvent for dissolving the

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magnesium compound and the nonmetallocene complex was changed to chloro toluene, the assistant chemical treating agent was changed to diethyl methyl aluminum ($Al(CH_3)(CH_3CH_2)_2$), and the chemical treating agent was changed to tetraethyl zirconium ($Zr(CH_3CH_2)_4$).

In this example, the ratio by molar of the magnesium compound to the nonmetallocene complex was 1:0.10, the ratio by weight of the magnesium compound to the porous carrier was 1:10, the ratio by molar of the magnesium compound to the assistant chemical treating agent was 1:0.10, and the ratio by molar of the magnesium compound to the chemical treating agent was 1:0.10.

The thus obtained supported nonmetallocene catalyst was named as CAT-IV-2-5.

Reference Example IV-1-A

Substantially the same as the Example IV-1, except for the following changes:

No nonmetallocene complex was used.

The thus obtained catalyst was named as CAT-IV-1-A.

Reference Example IV-1-B

Substantially the same as the Example IV-1, except for the following changes:

The ratio by molar of magnesium chloride to the nonmetallocene complex was changed to 1:0.14.

The thus obtained catalyst was named as CAT-IV-1-B.

Reference Example IV-1-C

Substantially the same as the Example IV-1, except for the following changes:

The ratio by molar of magnesium chloride to the nonmetallocene complex was changed to 1:0.03.

The thus obtained catalyst was named as CAT-IV-1-C.

Reference Example IV-1-D

Substantially the same as the Example IV-1, except for the following changes:

The composite carrier was not treated by titanium tetrachloride.

The thus obtained catalyst was named as CAT-IV-1-D.

Example IV-3

Application Example

The catalysts CAT-IV-1, CAT-IV-2, CAT-IV-1-1 to CAT-IV-1-5, CAT-IV-2-5, CAT-IV-1-A to CAT-IV-1-D obtained from the aforesaid Example IV series were used for ethylene homopolymerization/copolymerization and ultra high molecular weight polyethylene preparation under the following conditions according to the following processes respectively.

Homopolymerization: an autoclave for polymerization (5 L), a slurry polymerization process, hexane (2.5 L) as the solvent, a total polymerization pressure of 0.8 MPa, a polymerization temperature of 85° C., a partial pressure of hydrogen gas of 0.2 MPa, a polymerization time of 2 hours.

Specifically, 2.5 L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, 50 mg of a mixture of the supported nonmetallocene catalyst and the co-catalyst was added thereto, and then hydrogen gas was supplied thereto till 0.2 MPa, and finally ethylene was con-

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tinuously supplied thereto to keep the total polymerization pressure constant at 0.8 MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table IV-1.

Copolymerization: an autoclave for polymerization (5 L), a slurry polymerization process, hexane (2.5 L) as the solvent, a total polymerization pressure of 0.8 MPa, a polymerization temperature of 85° C., a partial pressure of hydrogen gas of 0.2 MPa, a polymerization time of 2 hours.

Specifically, 2.5 L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, 50 mg of a mixture of the supported nonmetallocene catalyst and the co-catalyst was added thereto. Hexene-1 (50 g) was added thereto all at once as the comonomer, and then hydrogen gas was supplied thereto till 0.2 MPa, and finally ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 0.8 MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the

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atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table IV-1.

Preparation of ultra high molecular weight polyethylene: an autoclave for polymerization (5 L), a slurry polymerization process, hexane (2.5 L) as the solvent, a total polymerization pressure of 0.5 MPa, a polymerization temperature of 70° C., a ratio by molar of the co-catalyst to the active metal in the catalyst of 100, a polymerization time of 6 hours.

Specifically, 2.5 L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, 50 mg of a mixture of the supported nonmetallocene catalyst and the co-catalyst was added thereto, and finally ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 0.5 MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table IV-2.

TABLE IV-1

The results of the olefin polymerization obtained with the supported nonmetallocene catalysts							
Experiment No.	Catalyst No.	Co-catalyst	ratio by molar of co-catalyst to active metal	type	Poly activity (kgPE/gCat)	Bulk density (g/cm ³)	Molecular weight distribution
1	CAT-IV-1	triethyl aluminum	100	homopolymerization	5.83	0.31	3.04
2	CAT-IV-1	methyl aluminoxane	100	homopolymerization	4.47	0.33	2.67
3	CAT-IV-1	triethyl aluminum	100	copolymerization	8.71	0.33	3.26
4	CAT-IV-1	triethyl aluminum	500	copolymerization	8.99	0.33	3.11
5	CAT-IV-1-1	triethyl aluminum	100	homopolymerization	3.17	0.26	
6	CAT-IV-1-2	triethyl aluminum	100	homopolymerization	6.13	0.29	
7	CAT-IV-1-3	triethyl aluminum	100	homopolymerization	3.19	0.27	
8	CAT-IV-1-4	triethyl aluminum	100	homopolymerization	2.44	0.26	
9	CAT-IV-1-5	triethyl aluminum	100	homopolymerization	5.86	0.30	
10	CAT-IV-2	triethyl aluminum	100	homopolymerization	5.15	0.33	2.82
11	CAT-IV-2	methyl aluminoxane	100	homopolymerization	4.19	0.35	2.50
12	CAT-IV-2	triethyl aluminum	100	copolymerization	6.74	0.32	3.07
13	CAT-IV-2-1	triethyl aluminum	100	homopolymerization	3.37	0.27	
14	CAT-IV-2-2	triethyl aluminum	100	homopolymerization	5.39	0.30	
15	CAT-IV-2-3	triethyl aluminum	100	homopolymerization	3.85	0.29	
16	CAT-IV-2-4	triethyl aluminum	100	homopolymerization	2.90	0.28	
17	CAT-IV-2-5	triethyl aluminum	100	homopolymerization	4.63	0.31	
18	CAT-IV-1-A	triethyl aluminum	100	homopolymerization	5.54	0.31	4.54
19	CAT-IV-1-B	triethyl aluminum	100	homopolymerization	7.77	0.34	2.73
20	CAT-IV-1-C	triethyl aluminum	100	homopolymerization	5.05	0.30	3.67
21	CAT-IV-1-D	triethyl aluminum	100	homopolymerization	1.10	0.26	2.52

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TABLE IV-2

The results of the ultra high molecular weight polyethylene preparation obtained with the supported nonmetallocene catalysts					
Experiment No.	Catalyst No.	Co-catalyst	Poly activity (kgPE/gCat)	Bulk density (g/cm ³)	Mv (10 ⁴ g/mol)
1	CAT-IV-1	triethyl aluminum	8.27	0.36	440
2	CAT-IV-1	methyl aluminumoxane	7.47	0.38	512
3	CAT-IV-2	triethyl aluminum	7.72	0.37	474
4	CAT-IV-2	methyl aluminumoxane	9.64	0.39	566
5	CAT-IV-1-A	triethyl aluminum	6.89	0.35	320
6	CAT-IV-1-B	triethyl aluminum	10.14	0.35	530
7	CAT-IV-1-C	triethyl aluminum	6.74	0.33	400
8	CAT-IV-1-D	triethyl aluminum	2.55	0.27	240

As can be seen from the results of the experiment Nos. 3 and 4 in the Table IV-1, increasing the amount of the co-catalyst to be used (i.e. increasing the ratio by molar of the co-catalyst to the active metal in the catalyst) will not significantly change the polymerization activity and the bulk density of the polymer. This fact indicates that a high activity for olefin polymerization can be obtained with a relatively less amount of the co-catalyst when the supported nonmetallocene catalyst produced in line with the process of this invention is used herein, and the resultant polymer product (for example polyethylene) exhibits superior polymer morphology and a high polymer bulk density.

Upon comparison of the results of the experiment No. 1 and those of the experiment No. 3, the results of the experiment No. 10 and those of the experiment No. 12, in the Table IV-1, it is clear that in case of copolymerization, the polymerization activity increases significantly. This fact indicates that the supported nonmetallocene catalyst produced in line with the process of this invention exhibits a relatively significant co-monomer effect.

Upon comparison of the results from the experiment No. 1 and those from the reference example experiment Nos. 18 to 21 in the Table IV-1, it is clear that the activity of the catalyst increases or decreases as the amount of the nonmetallocene complex to be introduced into the catalyst increases or decreases, while the molecular weight distribution of the polymer narrows or broadens accordingly. Further, the activity of the catalyst increases or decreases as the amount of the chemical treating agent to be introduced into the catalyst increases or decreases, while the molecular weight distribution of the polymer broadens or narrows accordingly. This fact indicates that the nonmetallocene complex shows a function of narrowing the molecular weight distribution of the polymer, while the chemical treating agent shows a function of increasing the activity of the catalyst and broadening the molecular weight distribution of the polymer. For this reason, different catalysts in terms of activity and polymer performances can be obtained with this invention by altering the ratio between these two components.

As can be seen from the Table IV-2, it is possible to prepare an ultra high molecular weight polyethylene (with to some degree increased bulk density) by using the catalyst according to this invention. Upon comparison of the results from the experiment No. 1 and those from the experiment No. 2, the results from the experiment No. 3 and those from the experi-

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ment No. 4, it is clear that the viscosity averaged molecular weight of the polymer can be increased by using MAO as the co-catalyst. Upon comparison of the results from the experiment No. 1 and those from the reference example experiment Nos. 5 to 8 in the Table IV-2, it is clear that the viscosity averaged molecular weight of the polymer increases or decreases as the amount of the nonmetallocene complex to be introduced into the catalyst increases or decreases. This fact indicates that the nonmetallocene complex further shows a function of increasing the viscosity averaged molecular weight of the polymer.

As can be seen from the results of the experiment Nos. 1, 18 and 21 in the Table IV-1 and those of the experiment Nos. 1, 5 and 8 in the Table IV-2, the catalyst obtained with the case wherein only nonmetallocene complex was used in preparation of the supported nonmetallocene catalyst, or that obtained with the case wherein only chemical treating agent was used in preparation of the supported nonmetallocene catalyst, shows lowered activity than that obtained with the case wherein both of the nonmetallocene complex and the chemical treating agent were used in preparation of the supported nonmetallocene catalyst. This fact indicates that the supported nonmetallocene catalyst produced in line with the process of this invention necessarily involves a synergic effect. That is, the activity observed with the case wherein both components exist is higher than that observed with the case wherein only either component exists.

It will be apparent to those skilled in the art that various modifications and variation can be made in the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

We claim:

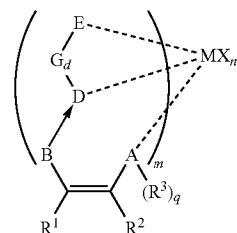
1. A process for producing a supported nonmetallocene catalyst, comprising:

dissolving at least one magnesium compound and at least one nonmetallocene complex in at least one solvent to obtain a magnesium compound solution;

mixing at least one carrier chosen from the group consisting of porous carriers and thermally activated porous carriers with the magnesium compound solution to obtain a slurry; and

drying the slurry or introducing into the slurry at least one precipitating agent to obtain the supported nonmetallocene catalyst,

wherein the nonmetallocene complex is chosen from the group consisting of the compounds having following formula,



wherein:

q is 0 or 1;

d is 1;

m is 1, 2 or 3;

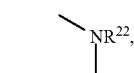
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M is chosen from the group consisting of metal atoms of Groups III to XI;

n is 1, 2, 3 or 4;

X is chosen from the group consisting of halogen atoms, a hydrogen atom, C₁-C₃₀ hydrocarbyl groups, substituted C₁-C₃₀ hydrocarbyl groups, oxygen-containing groups, nitrogen-containing groups, sulfur-containing groups, boron-containing groups, aluminum-containing groups, phosphor-containing groups, silicon-containing groups, germanium-containing groups, and tin-containing groups, when multiple Xs exist, the Xs may be the same as or different from one another, and may form a bond or a ring with one another;

A is chosen from the group consisting of an oxygen atom, a sulfur atom, a selenium atom,



—PR²⁸R²⁹, —P(O)R³⁰OR³¹, sulfone groups, sulfoxide groups, and —Se(O)R³⁹, wherein N, O, S, Se and P in A each represents a coordination atom;

B is chosen from the group consisting of a nitrogen atom, nitrogen-containing groups, phosphor-containing groups, and C₁-C₃₀ hydrocarbylene groups;

D is chosen from the group consisting of a nitrogen atom, an oxygen atom, a sulfur atom, a selenium atom, a phosphor atom, nitrogen-containing groups, phosphor-containing groups, C₁-C₃₀ hydrocarbylene group, sulfone group, sulfoxide groups,



and —P(O)R³²(OR³³), wherein N, O, S, Se and P in D each represents a coordination atom;

E is chosen from the group consisting of nitrogen-containing groups, oxygen-containing groups, sulfur-containing groups, selenium-containing groups, phosphor-containing groups, and cyano groups, wherein N, O, S, Se and P in E each represents a coordination atom;

G is chosen from the group consisting of C₁-C₃₀ hydrocarbylene groups, substituted C₁-C₃₀ hydrocarbylene groups, and inert functional groups;

→ represents a single bond or a double bond;

- represents a covalent bond or an ionic bond;

--- represents a coordination bond, a covalent bond or an ionic bond;

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R¹ to R³, R²² to R³³, and R³⁹ are each independently chosen from the group consisting of a hydrogen atom, C₁-C₃₀ hydrocarbyl groups, substituted C₁-C₃₀ hydrocarbyl groups, and inert functional groups, wherein these groups may be identical to or different from one another, and any adjacent groups may form a bond or a ring with one another.

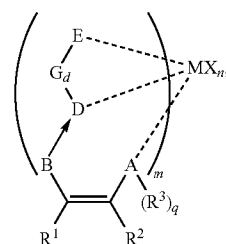
2. A process for producing a supported nonmetallocene catalyst, comprising:

dissolving at least one magnesium compound and at least one nonmetallocene complex in at least one solvent to obtain a magnesium compound solution;

mixing at least one carrier chosen from the group consisting of porous carriers and thermally activated porous carriers with the magnesium compound solution to obtain a slurry;

drying the slurry or introducing into the slurry at least one precipitating agent to obtain a composite carrier; and treating the composite carrier with at least one chemical treating agent chosen from the group consisting of Group IVB metal compounds to obtain the supported nonmetallocene catalyst,

wherein the nonmetallocene complex is chosen from the group consisting of the compounds having following formula,



wherein:

q is 0 or 1;

d is 1;

m is 1, 2 or 3;

M is chosen from the group consisting of metal atoms of Groups III to XI;

n is 1, 2, 3 or 4;

X is chosen from the group consisting of halogen atoms, a hydrogen atom, C₁-C₃₀ hydrocarbyl groups, substituted C₁-C₃₀ hydrocarbyl groups, oxygen-containing groups, nitrogen-containing groups, sulfur-containing groups, boron-containing groups, aluminum-containing groups, phosphor-containing groups, silicon-containing groups, germanium-containing groups, and tin-containing groups, when multiple Xs exist, the Xs may be the same as or different from one another, and may form a bond or a ring with one another;

A is chosen from the group consisting of an oxygen atom, a sulfur atom, a selenium atom,



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—PR²⁸R²⁹, —P(O)R³⁰OR³¹, sulfone groups, sulfoxide groups, and —Se(O)R³⁹, wherein N, O, S, Se and P in A each represents a coordination atom;

B is chosen from the group consisting of a nitrogen atom, nitrogen-containing groups, phosphor-containing groups, and C₁-C₃₀ hydrocarbylene groups;

D is chosen from the group consisting of a nitrogen atom, an oxygen atom, a sulfur atom, a selenium atom, a phosphor atom, nitrogen-containing groups, phosphor-containing groups, C₁-C₃₀ hydrocarbylene group, sulfone group, sulfoxide groups,



and —P(O)R³²(OR³³), wherein N, O, S, Se and P in D each represents a coordination atom;

E is chosen from the group consisting of nitrogen-containing groups, oxygen-containing groups, sulfur-containing groups, selenium-containing groups, phosphor-containing groups, and cyano groups, wherein N, O, S, Se and P in E each represents a coordination atom;

G is chosen from the group consisting of C₁-C₃₀ hydrocarbylene groups, substituted C₁-C₃₀ hydrocarbylene groups, and inert functional groups;

→ represents a single bond or a double bond;

- represents a covalent bond or an ionic bond;

--- represents a coordination bond, a covalent bond or an ionic bond;

R¹ to R³, R²² to R³³, and R³⁹ are each independently chosen from the group consisting of a hydrogen atom, C₁-C₃₀ hydrocarbyl groups, substituted C₁-C₃₀ hydrocarbyl groups, and inert functional groups, wherein these groups may be identical to or different from one another, and any adjacent groups may form a bond or a ring with one another.

3. The process according to claim 2, further comprising pre-treating the composite carrier with at least one assistant chemical treating agent chosen from the group consisting of aluminoxanes and alkylaluminums before treating the composite carrier with the at least one chemical treating agent.

4. The process according to claim 1 or 2, wherein the at least one carrier is chosen from the group consisting of olefin homopolymers or copolymers, vinyl alcohol homopolymers or copolymers, cyclodextrins, polyesters or co-polyesters, polyamides or co-polyamides, vinyl chloride homopolymers or copolymers, acrylic ester homopolymers or copolymers, methacrylic ester homopolymers or copolymers, styrene homopolymers or copolymers, partly crosslinked products of these homopolymers or copolymers, refractory oxides or refractory composite oxides of a Group IIA, IIIA, IVA or IVB metal, clay, molecular sieve, mica, montmorillonite, bentonite and kieselguhr.

5. The process according to claim 4, wherein the at least one is chosen from the group consisting of partly crosslinked styrene polymers, silica, alumina, magnesia, silica-alumina, magnesia-alumina, titanium oxide, molecular sieve and montmorillonite.

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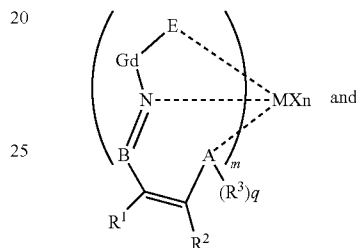
6. The process according to claim 1 or 2, wherein the at least one magnesium compound is chosen from the group consisting of magnesium halides, alkoxy magnesium halides, alkoxy magnesiums, alkyl magnesiums, alkyl magnesium halides and alkyl alkoxy magnesiums.

7. The process according to claim 6, wherein the at least one magnesium compound is chosen from the group consisting of magnesium halides.

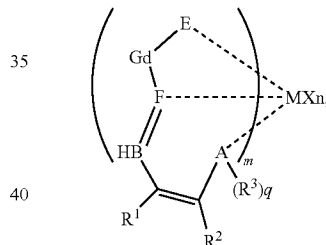
8. The process according to claim 1 or 2, wherein the at least one solvent is chosen from the group consisting of C₆₋₁₂ aromatic hydrocarbons, halogenated C₆₋₁₂ aromatic hydrocarbons, esters and ethers.

9. The process according to claim 1 or 2, wherein the at least one nonmetallocene complex is chosen from the group consisting of compound (A) and compound (B),

(A)



(B)

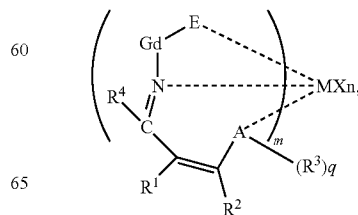


wherein,

F is chosen from the group consisting of a nitrogen atom, nitrogen-containing groups, oxygen-containing groups, sulfur-containing groups, selenium-containing groups and phosphor-containing groups, wherein N, O, S, Se and P in F each represents a coordination atom.

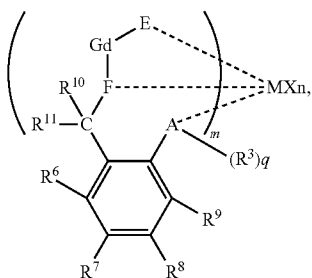
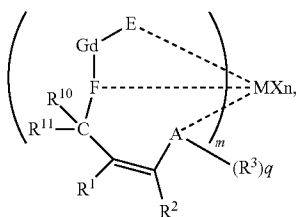
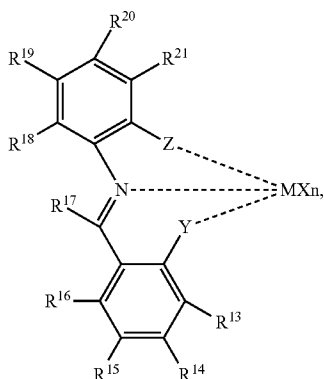
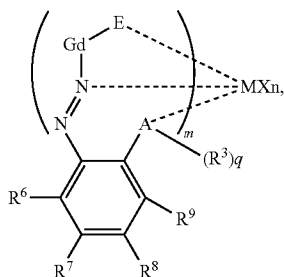
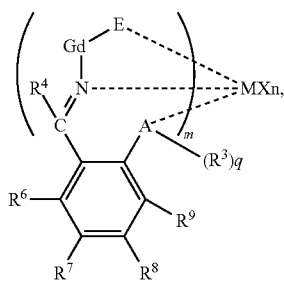
10. The process according to claim 9, wherein the at least one nonmetallocene complex is chosen from the group consisting of compound (A-1), compound (A-2), compound (A-3), compound (A-4), compound (B-1), compound (B-2), compound (B-3), and compound (B-4),

(A-1)



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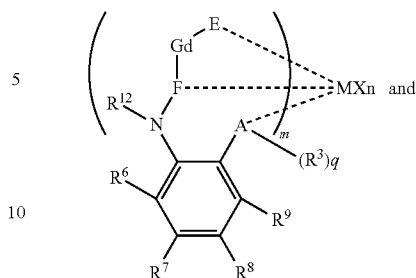
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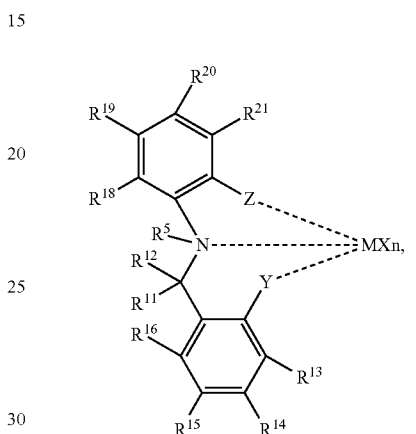
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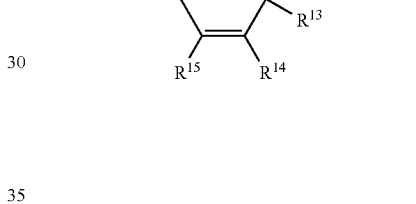
(A-2)



(A-3)



(A-4)



wherein,

Y is chosen from the group consisting of an oxygen atom, nitrogen-containing groups, oxygen-containing groups, sulfur-containing groups, selenium-containing groups and phosphor-containing groups, wherein N, O, S, Se and P in Y each represents a coordination atom;

Z is chosen from the group consisting of nitrogen-containing groups, oxygen-containing groups, sulfur-containing groups, selenium-containing groups, phosphor-containing groups and cyano groups, wherein N, O, S, Se and P in Z each represents a coordination atom;

R⁴, and R⁶ to R²¹ are each independently chosen from the group consisting of a hydrogen atom, C₁-C₃₀ hydrocarbyl groups, substituted C₁-C₃₀ hydrocarbyl groups and inert functional groups, wherein these groups may be identical to or different from one another, and any adjacent groups may form a bond or a ring with one another; and

R⁵ is chosen from the group consisting of a lone pair electron on a nitrogen atom, a hydrogen atom, C₁-C₃₀ hydrocarbyl groups, substituted C₁-C₃₃ hydrocarbyl groups, oxygen-containing groups, sulfur-containing groups, nitrogen-containing groups, selenium-containing groups, and phosphor-containing groups, with the proviso that when R⁵ is chosen from the group consisting of oxygen-containing groups, sulfur-containing groups, nitrogen-containing groups, selenium-containing groups and phosphor-containing groups, N, O, S, P and Se in the R⁵ each can act as a coordination atom.

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11. The process according to claim 10, wherein, the halogen atom is chosen from the group consisting of F, Cl, Br and I,

the nitrogen-containing groups are chosen from the group consisting of



—NR²³R²⁴, and —T-NR²³R²⁴,

the phosphor-containing groups are chosen from the group consisting of



—PR²⁸R²⁹, —P(O)R³⁰R³¹ and —P(O)R³²(OR³³),

the oxygen-containing groups are chosen from the group consisting of hydroxy, —OR³⁴ and —T-OR³⁴,

the sulfur-containing groups are chosen from the group consisting of —SR³⁵, —T-SR³⁵, —S(O)R³⁶ and —T-SO₂R³⁷,

the selenium-containing groups are chosen from the group consisting of —SR³⁸, —T-SeR³⁸, —Se(O)R³⁹ and —T-Se(O)R³⁹,

the group T is chosen from the group consisting of C₁-C₃₀ hydrocarbylene groups, substituted C₁-C₃₀ hydrocarbylene groups and inert functional groups,

R³⁷ is chosen from the group consisting of a hydrogen atom, C₁-C₃₀ hydrocarbyl groups, substituted C₁-C₃₀ hydrocarbyl groups and inert functional groups,

the C₁-C₃₀ hydrocarbyl groups are chosen from the group consisting of C₁-C₃₀ alkyl groups, C₇-C₅₀ alkylaryl groups, C₇-C₅₀ aralkyl groups, C₃-C₃₀ cyclic alkyl groups, C₂-C₃₀ alkenyl groups, C₂-C₃₀ alkynyl groups, C₆-C₃₀ aryl groups, C₈-C₃₀ fused-ring groups and C₄-C₃₀ heterocycle groups, wherein the C₄-C₃₀ heterocycle group contains 1 to 3 hetero atom(s) chosen from the group consisting of a nitrogen atom, an oxygen atom and a sulfur atom,

the substituted C₁-C₃₀ hydrocarbyl groups are chosen from the group consisting of hydrocarbyl groups having at least one substituent chosen from the group consisting of halogen atoms and C₁-C₃₀ alkyl groups,

the inert functional groups are chosen from the group consisting of halogen atoms, oxygen-containing groups, nitrogen-containing groups, silicon-containing groups, germanium-containing groups, sulfur-containing groups, tin-containing groups, C₁-C₁₀ ester groups and nitro groups,

the boron-containing groups are chosen from the group consisting of BF₄⁻, (C₆F₅)₄B⁻ and (R⁴⁰BAR₃)⁻,

the aluminum-containing groups are chosen from the group consisting of AlPh₄⁻, AlBr₄⁻, AlCl₄⁻, AlBr₄⁻, AlI₄⁻ and R⁴¹AlAr₃⁻,

the silicon-containing groups are chosen from the group consisting of —SiR⁴²R⁴³R⁴⁴, and —T-SiR⁴⁵,

the germanium-containing groups are chosen from the group consisting of —GeR⁴⁶R⁴⁷R⁴⁸ and —T-GeR⁴⁹,

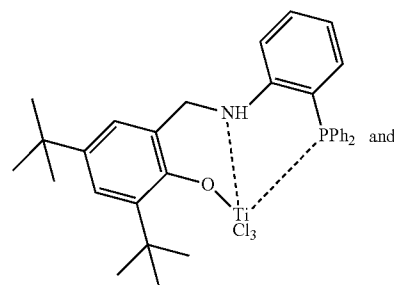
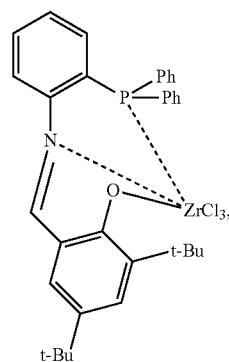
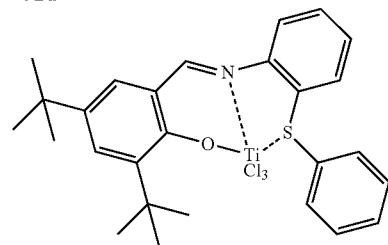
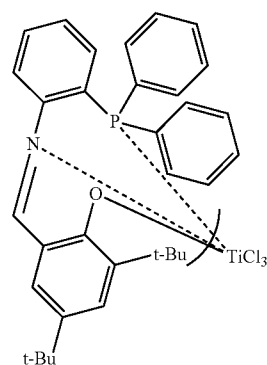
the tin-containing groups are chosen from the group consisting of —SnR⁵⁰R⁵¹R⁵², —T-SnR⁵³ and —T-Sn(O)R⁵⁴,

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the Ar is chosen from the group consisting of C₆-C₃₀ aryl groups,

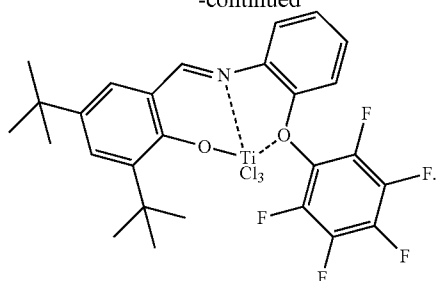
R³⁴ to R³⁶, R³⁸ and R⁴⁰ to R⁵⁴ are each independently chosen from the group consisting of a hydrogen atom, C₁-C₃₀ hydrocarbyl groups, substituted C₁-C₃₀ hydrocarbyl groups and inert functional groups, wherein these groups may be identical to or different from one another, and any adjacent groups may form a bond or a ring with one another.

12. The process according to claim 1 or 2, wherein the at least one nonmetallocene complex is chosen from the group consisting of:



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-continued



13. The process according to claim 1, wherein molar ratio of the at least one magnesium compound (based on Mg) to the at least one nonmetallocene complex is 1:0.01-1, ratio of the at least one magnesium compound to the at least one solvent is 1 mol:75-400 ml, weight ratio of the at least one magnesium compound (on a solid basis) to the at least one carrier is 1:0.1-20, and volume ratio of the at least one precipitating agent to the at least one solvent is 1:0.2-5.

14. The process according to claim 2, wherein molar ratio of the at least one magnesium compound (based on Mg) to the at least one nonmetallocene complex is 1:0.01-1, ratio of the at least one magnesium compound to the at least one solvent is 1 mol:75-400 ml, weight ratio of the at least one magnesium compound (on a solid basis) to the at least one carrier is 1:0.1-20, volume ratio of the at least one precipitating agent to the at least one solvent is 1:0.2-5, and molar ratio of the at least one magnesium compound (based on Mg) to the at least one chemical treating agent (based on the Group IVB metal) is 1:0.01-1.

15. The process according to claim 1 or 2, wherein the at least one precipitating agent is chosen from the group consisting of alkanes, cyclic alkanes, halogenated alkanes and halogenated cyclic alkanes.

16. The process according to claim 15, wherein the at least one precipitating agent is chosen from the group consisting of pentane, hexane, heptane, octane, nonane, decane, cyclohexane, cyclopentane, cycloheptane, cyclodecane, cyclononane, dichloromethane, dichloro hexane, dichloro heptane,

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trichloro methane, trichloro ethane, trichloro butane, dibromo methane, dibromo ethane, dibromo heptane, tribromo methane, tribromo ethane, tribromo butane, chlorinated cyclopentane, chlorinated cyclohexane, chlorinated cycloheptane, chlorinated cyclooctane, chlorinated cyclononane, chlorinated cyclodecane, brominated cyclopentane, brominated cyclohexane, brominated cycloheptane, brominated cyclooctane, brominated cyclononane and brominated cyclodecane.

17. The process according to claim 2, wherein the Group IVB metal compounds are chosen from the group consisting of Group IVB metal halides, Group IVB metal alkylates, Group IVB metal alkoxylates, Group IVB metal alkyl halides, and Group IVB metal alkoxy halides.

18. The process according to claim 17, wherein the Group IVB metal compounds are chosen from the group consisting of Group IVB metal halides.

19. The process according to claim 3, wherein the aluminoxanes are chosen from the group consisting of methyl aluminoxane, ethyl aluminoxane, isobutyl aluminoxane and n-butyl aluminoxane, and the alkylaluminum is one or more selected from the group consisting of trimethyl aluminum, triethyl aluminum, tripropyl aluminum, triisobutyl aluminum, tri-n-butyl aluminum, triisooamyl aluminum, tri-n-amyl aluminum, trihexyl aluminum, tri-iso-hexyl aluminum, diethyl methyl aluminum and ethyl dimethyl aluminum.

20. The process according to claim 3, wherein molar ratio of the at least one magnesium compound (based on Mg) to the at least one assistant chemical treating agent (based on Al) is 1:0-1.0.

21. A supported nonmetallocene catalyst, produced according to the process of claim 1 or 2.

22. An olefin homopolymerization/copolymerization process comprising polymerizing at least one olefin in the presence of the supported nonmetallocene catalyst according to claim 21 with at least one co-catalyst chosen from the group consisting of aluminoxanes, alkylaluminums, halogenated alkyl aluminums, fluoroboranes, alkylborons and alkylboron ammonium salts.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 8,952,112 B2
APPLICATION NO. : 13/503825
DATED : February 10, 2015
INVENTOR(S) : Chuanfeng Li et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In The Claims

Claim 1, Col. 89, Line 65, “-” should read as -- — --.

Claim 2, Col. 91, Line 36, “-” should read as -- — --.

Claim 5, Col. 91, Line 64, “one is” should read as --one carrier is--.

Claim 11, Col. 95, Line 48, “of hydrocarbyl” should read as --of C₁-C₃₀ hydrocarbyl--.

Claim 11, Col. 95, Line 60, “AlPh₄⁻, AlBr₄⁻” should read as --AlPh₄⁻, AlF₄⁻--.

Signed and Sealed this
Thirtieth Day of June, 2015



Michelle K. Lee
Director of the United States Patent and Trademark Office